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## (54) INK JET RECORDING PAPER

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To realize high image quality recording through quick absorption of ink by providing a layer containing a mordant for fixing a water soluble dye and an air gap layer having an air gap capacity higher than a specific ratio of the maximum ink delivery on a support substantially absorbing no water.

**SOLUTION:** A layer containing a mordant for fixing a water soluble dye is provided on a support substantially absorbing no water. An air gap layer having an air gap capacity higher than 90% of the maximum ink delivery is provided on the side farther from the support than the layer containing a mordant. When the air gap layer is provided at the uppermost layer farthest from the support, the advantage of the air gap for absorbing ink quickly can be utilized to the maximum. When the binder in the layer containing a mordant is a hard film, water resistance can be enhanced for a large quantity of water. When the binder is an unhardened film, swelled binder intrudes into the upper air gap layer at the time of absorbing ink to choke the air gap thus lowering ink absorption.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The ink jet record form with which it has the opening layer prepared at the side which is separated from a base material from the mordant content layer and this mordant content layer which fix water soluble dye on the base material which does not absorb water at all substantially, and void volume of this opening layer is characterized by the thing of an ink maximum delivery which it has 90% or more.

[Claim 2] The ink jet record form according to claim 1 characterized by the furthest layer from a base material being an opening layer.

[Claim 3] The ink jet record form according to claim 1 or 2 characterized by carrying out the dura mater of the binder of a mordant content layer.

[Claim 4] The ink jet record form according to claim 1, 2, or 3 characterized by a mordant being a tertiary amine system polymer or a quarternary-ammonium-salt system polymer.

[Claim 5] The ink jet record form according to claim 4 characterized by containing acid-treatment gelatin in a mordant content layer.

[Claim 6] The ink jet record form according to claim 4 or 5 characterized by containing an image stabilizer in a mordant content layer.

[Claim 7] The ink jet record form according to claim 4, 5, or 6 characterized by containing the compound which absorbs ultraviolet rays in the layer which is in a far side rather than a mordant content layer to a base material.

[Claim 8] An ink jet record form given in any 1 term of claims 1-7 characterized by the non-subtlety particle in an opening layer and the volume ratio of a binder being five or more.

[Claim 9] An ink jet record form given in any 1 term of claims 1-8 characterized by for an opening layer making an inorganic solid-state particle condense at the time of coating liquid preparation or coat formation, making the three-dimensional structure form, and obtaining it.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

**[0001]**

**[Field of the Invention]** This invention relates to the ink jet record form which has improved especially ink absorptivity about the ink jet record form which records using water soluble dye.

**[0002]**

**[Description of the Prior Art]** although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, it is comparatively alike and a high speed, the low noise, and multiple-color-izing are easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread quickly in various fields, such as various printers, facsimile, and a computer terminal, in current.

**[0003]** As a record form used by this ink jet recording method, when a printing dot laps [ that the concentration of a printing dot is high and a color tone is brightly skillful, and absorption of ink ] early, ink flows out or it spreads, or the diffusion to the longitudinal direction of not carrying out and a printing dot is not large beyond the need, and for the circumference to be smooth and not to fade etc. is demanded.

**[0004]** When especially ink rate of absorption is slow, in case the liquid ink drop of two or more colors laps and is recorded, in order to become nonuniformity, and for a mutual color to spread in the border area of a color which a drop causes a HAJIKI phenomenon on a record form, and is different and to be easy to reduce image quality greatly, it is required to have ink absorptivity high as a record form.

**[0005]** In order to solve these problems, very many techniques are proposed from the former. As the pigment in the record form which carried out humidity of the coating for surface treatment to the low size stencil indicated by JP,52-53012,A, the record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, and the clad layer indicated by JP,56-157,A The record form containing non-colloid silica powder, the record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The record form which has two hole distribution peaks indicated by JP,58-110287,A, The record form which consists of the vertical two-layer porous layer indicated by JP,62-111782,A, The record form which has the infinite form crack indicated by JP,59-68292,A, 59-123696, 60-18383, etc., The record form which has the impalpable powder layer indicated by JP,61-135786,A, 61-148092, 62-149475, etc., JP,63-252779,A, JP,1-108083,A, 2-136279, The record form containing the pigment which has the specific physical-properties value indicated by 3-65376, 3-27976, etc., or a particle silica, JP,57-14091,A, 60-219083, 60-210984, 61-20797, 61-188183, JP,5-278324,A, 6-92011, 6-183134, 7-137431, The record form containing particle silicas, such as a colloid silica indicated by 7-276789 etc., A large number, such as a record form containing the hydrated alumina particle indicated by JP,2-276671,A, 3-67684, 3-215082, 3-251488, 4-67986, 4-263983, 5-16517, etc., are known.

**[0006]** However, since many ink absorbing layers with many openings will have irregularity with micro interface with air and coat front face, the incident light to an ink absorbing layer is scattered

about or transparency is barred when an ink absorbing layer absorbs ink or it consists of only layers which have many openings for holding, it becomes or tends to be hard to come out opaquely lusterless.

[0007] Moreover, in order to form an opening, there is a fault out of which the smooth nature on the front face of a coat by own irregularity of a pigment or the irregularity of the secondary floc of a pigment falls, and gloss cannot come easily.

[0008] On the other hand, many ink jet record forms of the type which absorbs ink and is held in a swelling operation of the binder of an ink absorption layer are also known, without preparing an opening into a coat. For example, many the recording papers, films, etc. which applied hydrophilic binders, such as gelatin, casein, starch, an alginic acid, polyvinyl alcohol, various kinds of conversion polyvinyl alcohol, a polyvinyl pyrrolidone, polyethylene oxide, polypropylene oxide, a carboxymethyl cellulose, HIDOROKI ethyl cellulose, a dextran, and a pullulan, on the base material as binders are known from the former.

[0009] Although these record forms are inferior in ink absorptivity compared with the record form which has the above-mentioned opening, high glossiness and optical density, and a clear image are obtained, and they are useful as a high-definition record application.

[0010] The ink jet record form which carried out the laminating of the upper layer which changes from hydrophilic resin, a non-subtlety particle, and a bulking agent to the lower layer which changes from water soluble resin to JP,7-186521,A as what combined the above two types is indicated. Moreover, as it is in JP,61-12388,A, 61-35275, 61-49883, 61-49884, 61-49885, 61-135787, 61-135788, 62-196175, 62-222887, etc., the ink jet record form which prepared the ink transparency layer in the upper layer rather than the ink maintenance layer is known.

[0011] since a coloring matter molecule existed between the inside of a binder, and an opening independently unlike the color photographic paper in which a coloring matter molecule be distribute in the state of a high-concentration particle in oils, a fault which waterdrop be pour on a recording surface, or coloring matter spread when it be save under high humidity conditions the printing back for a long period of time, or be easy flow out be in various kinds of ink jet record forms suitable for the water-soluble above-mentioned ink.

[0012] In order to improve the water resisting property and moisture resistance of this coloring matter, the various methods of making coloring matter fix in a binder from the former are proposed. Especially an effective means is the approach of adding as a particle latex by using as a uniform water solution the polymer which has the nitrogen atom of the 3rd class or the 4th class.

[0013] For example, the ink jet record form applied on the stencil or the polyethylene terephthalate (PET) film base material by using as an ink absorbing layer the coating liquid which contains a basic mordant for gelatin as some binders is indicated by JP,57-36692,A.

[0014] Moreover, the water-color-ink record form which made JP,53-49113,A carry out impregnation of the polyethyleneimine into paper; in JP,58-24492,A The record ingredient which has the electrolyte polymer which has a cation or an anion radical; to JP,63-224988,A The charge of a recorded material which contains the 1st class - tertiary amine, or quarternary ammonium salt in an ink absorbing layer, and has pH of an ink maintenance layer in 2-8; to JP,63-307979,A The ink jet record sheet which has a layer containing the hydrophilic polymer mordant which has the 3rd class or the 4th class nitrogen atom, and the polymer which has a hydrophilic radical; to JP,59-198186,A and 59-198188 The charge of a recorded material which made the organic base of polyethyleneimine contain in the coating layer in a base material or on a base material; to JP,60-46288,A The ink jet record approach using the ink containing a specific color, and the record ingredient containing polyamine etc.; JP,61-61887,A, To 61-72581, 61-252189, and 62-174184 The ink jet record form containing the poly allylamine; to JP,61-172786,A the polymer which has an intermolecular hydrogen bridge, and the polymer (a polyethylene glycol —) which does not have a hydrogen bond nature machine among molecules (gelatin, polyethyleneimine, etc.) The ink jet record ingredient containing a polyvinyl pyrrolidone etc.; to JP,63-162275,A A cationic polymer and a cationic surface active agent on a base material to spreading or ink jet record form; JP,6-143798,A which carried out impregnation The record sheet which superimposed the color fixation layer which uses a quarternary-ammonium-salt polymerization object and cation conversion polyvinyl alcohol as a principal component on a plastics base material, and the color transparency and ink absorption

layer which were prepared on it is indicated.

[0015] Generally it is [ causing thickening and condensation in many cases ] difficult during preparation / spreading to include a polymer with such color fixing ability in an opening layer. Moreover, even if it incorporates, in order that a color may fix in an opening layer, there is an inclination for a color to be exposed to the oxygen in air and to degrade lightfastness. It was rare to include a polymer with color fixing ability in an opening layer conventionally from these reasons.

[0016] It is possible to, incorporate the polymer which has the above-mentioned color fixing ability comparatively easily about the ink jet record form of the type which absorbs ink and is held in a swelling operation of the binder of an ink absorption layer, without preparing an opening into a coat on the other hand. However, it is a problem as above-mentioned that the layer which consists of this type of water-soluble binder has the late absorptivity of ink.

[0017]

[Problem(s) to be Solved by the Invention] The object of this invention is in the improvement of an ink jet record form which used water soluble dye, the high definition record by absorption of quick ink is possible, the water resisting property and moisture resistance of a color after record are improved [ this invention is made in view of the above-mentioned actual condition, ], and it is in offering the ink jet record form in which lightfastness moreover is not reduced.

[0018]

[Means for Solving the Problem] The object of above-mentioned this invention is attained by the following configurations.

[0019] (1) The ink jet record form which has the opening layer prepared at the side which is separated from a base material from the mordant content layer and this mordant content layer which fix water soluble dye on the base material which does not absorb water at all substantially, and an ink maximum delivery has [ the void volume of this opening layer ] 90% or more.

[0020] (2) An ink jet record form given in (1) whose furthest layer from a base material is an opening layer.

[0021] (3) (1) to which the dura mater of the binder of a mordant content layer is carried out, or an ink jet record form given in (2).

[0022] (4) (1) whose a mordant is a tertiary amine system polymer or a quaternary-ammonium-salt system polymer, (2), or an ink jet record form given in (3).

[0023] (5) An ink jet record form given in (4) which contains acid-treatment gelatin in a mordant content layer.

[0024] (6) (4) which contains an image stabilizer in a mordant content layer, or an ink jet record form given in (5).

[0025] (7) (4) containing the compound which absorbs ultraviolet rays in the layer which is in a far side rather than a mordant content layer to a base material, (5), or an ink jet record form given in (6).

[0026] (8) An ink jet record form given in any 1 term of (1) - (7) the non-subtlety particle in an opening layer and whose volume ratio of a binder are five or more.

[0027] (9) The opening layer made the inorganic solid-state particle condense at the time of coating liquid preparation or coat formation, made the three-dimensional structure form, and was obtained, and it is an ink jet record form given in any 1 term of (1) - (8).

[0028] Hereafter, this invention is explained more to a detail.

[0029] The opening layer which the ink jet record form used for this invention has consists of the opening formed solid-state components, such as a hydrophilic property or a hydrophobic binder, an inorganic or organic particle, or an oil droplet, and between them.

[0030] It is common that the solid-state components which can perform formation of an opening by various methods and an opening layer contains by the approach also differ. The formation approach of a typical opening layer is explained below.

[0031] The uniform coating liquid containing two or more sorts of polymers is applied on a base material. \*\* In a desiccation process The coating liquid containing the approach \*\* solid-state particle and hydrophilic property, or hydrophobic binder which is made to carry out phase separation of these polymers mutually, and forms an opening is immersed in the liquid which contains water or a suitable organic solvent for a record form after spreading / desiccation at a

base material top. In a desiccation process after applying the coating liquid containing the compound which has the property which foams at the time of the approach \*\* coat formation which is made to dissolve a solid-state particle and creates an opening The coating liquid containing the approach \*\* porosity solid-state particle and the hydrophilic binder which this compound is made to foam and form an opening into a coat is applied on a base material. As opposed to the approach \*\* hydrophilic-property binder which forms an opening between the inside of a porosity particle, or a particle The coating liquid containing the solid-state particle and/or particle oil droplet which have the volume more than equivalent weight (preferably 1.0 or more times) in general, and a hydrophilic binder is applied on a base material. Between solid-state particles The approach the approach \*\* mean particle diameter which creates an opening makes solid-state particle about 0.1 micrometers or less condense at the time of coating liquid preparation or coat formation, forms a secondary particle or the three-dimensional structure, and creates an opening.

[0032] As for the opening formation approach in this invention, it is desirable to use the approach of not much not reducing the glossiness on the front face of the recording paper, with any above-mentioned means, although it is good. About 0.5 micrometers, the magnitude of an opening for that is about 0.2 micrometers or less, and it is preferably desirable to set up so that the magnitude of packing and the manufacture conditions at the time of coat formation may also turn into conditions which form such an opening especially preferably about 0.3 micrometers.

[0033] The approach of creating without taking a complicated production process from a viewpoint referred to as creating an ink jet record form by low cost on the other hand is desirable.

[0034] The desirable methods of hitting carrying out this invention from the above viewpoint are the above-mentioned \*\*, \*\*, and \*\*, and especially a desirable thing is the approach of \*\* or \*\*.

[0035] The total amount of the void volume of the opening layer of the ink jet record form used for this invention needs to be 90% or more of the maximum delivery of ink. Even when the layer containing a mordant is in the upper layer from an opening layer unlike this invention, and the void volume of an opening layer does not fulfill 90% of the maximum delivery of ink, the problem which ink overflows and worsens drying in the case of printing of the high amount of ink is not produced. However, only within the case where it is in the upper layer rather than the layer in which an opening layer contains a mordant, ink overflows in the case of printing of the high amount of ink, image quality is reduced or problems, like drying [ after printing ] is late arise.

[0036] Void volume is the value which deducted the total amount of the capacity of solid content, such as a binder in an opening layer, and various kinds of bulking agents, from the desiccation thickness in an opening layer, and voidage shows the rate of the amount of openings to the capacity of these solid content here.

[0037] It is good to carry out voidage preferably more than 250 capacity %. Although the upper limit of voidage generally changes with the class of bulking agent, or the classes of binder, generally it is below 400 capacity % from the reinforcement as a coat, brittleness, etc.

[0038] When there is an opening layer in the opening layer containing a solid-state particle, as a solid-state particle, a well-known solid-state particle inorganic [ various kinds of ] or organic can be conventionally used in an ink jet record form.

[0039] As an example of the above-mentioned inorganic particle, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, diatomaceous earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide, etc. can be mentioned. Such a non-subtlety particle may be added in the condition of having been used after homogeneity had distributed in the binder with the primary particle, and having formed secondary floc, and having distributed in the binder.

[0040] On the other hand, as an example of an organic particle, polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, melamine resin, etc. are mentioned.

[0041] In this invention, it is more desirable than the point of high concentration being attained, and

a clear image being recorded and being able to manufacture by low cost to use the solid-state particle chosen from a hydrated alumina particle, a silica particle, and a calcium carbonate as a solid-state particle.

[0042] The alumina or hydrated alumina used preferably is the porosity alumina whose sum of the pore volume whose radius is 3–10nm is 0.2 – 2 cc/g, or its hydrated compound. The measurement means of pore volume can be measured with a well-known nitrogen adsorption process to an alumina or the desiccation solid content of hydrated alumina.

[0043] An alumina or hydrated alumina may be crystallinity, or may be amorphous, and a configuration can use the thing of the configuration of arbitration, such as an infinite form particle, a spherical particle, and a needlelike particle.

[0044] Silicas of the configuration of arbitration, such as a synthetic silica which could use various kinds of well-known silica system particles by the ink jet conventionally, for example, was compounded by wet or the gaseous-phase method as a silica system particle used for this invention, colloidal silica, and a porosity silica which a primary particle condenses and forms the secondary particle, can be used. As such an example, for example, the synthetic amorphous silica indicated by JP,55–51583,A, 56–148583, etc., The silica ultrafine particle compounded by the gaseous-phase method indicated by JP,60–204390,A, The synthetic infinite form silica containing the fluorine indicated by JP,60–222282,A, The synthetic infinite form silica in which surface treatment was carried out by the silane coupling agent indicated by JP,60–224580,A and 62–178384, The spherical silica indicated by JP,62–183382,A and 63–104878, The synthetic silica particle whose Na<sub>2</sub>O content indicated by JP,63–317381,A is 0.5 % of the weight or more, The specific surface area indicated by JP,1–115677,A The synthetic silica particle more than 100m<sup>2</sup>/g, The synthetic silica particle which was indicated by JP,62–286787,A and by which alumina surface treatment was carried out, The synthetic silica particle by which surface treatment was carried out by calcium and Mg which were indicated by JP,1–259982,A, or Ba, The colloidal silica oil absorption was indicated to be by 180cc[/g ] or more k composition silica particle and JP,57–14091,A, The cationic colloidal silica indicated by JP,60–219084,A, JP,6–92011,A, 6–297830, and 7–81214, Connection/or branched colloidal silica can be mentioned in the shape of [ which was indicated by JP,5–278324,A and 7–81214 ] a rosary.

[0045] However, in order to obtain high glossiness and high void volume, it is desirable to use the silica ultrafine particle whose mean particle diameter is 7–30nm. Cation conversion of the front face could be carried out, and this silica particle could be processed by aluminum, calcium, Mg, Ba, etc.

[0046] As a calcium carbonate used for the record form of this invention For example, JP,5712–486,A, 57–129778, 58–55283, The precipitated calcium carbonate which has specific surface area in the specification indicated by 61–20792, The needle pillar-shaped calcium carbonate indicated by JP,63–57277,A and JP,4–250091,A, The calcium-carbonate particle which the specific needlelike primary particle indicated by JP,3–251487,A condensed, and formed the secondary particle, the needle which has the specific oil absorption indicated by JP,4–250091,A and 4–260092 — a pillar-shaped prismatic crystal Argo night calcium carbonate, the spherical precipitated calcium carbonate indicated by JP,7–40648,A are mentioned. Since high glossiness and high void volume can be obtained, it is desirable that particle size uses calcium-carbonate particle about 0.1 micrometers or less, and the activity of the calcium-carbonate particle especially whose mean particle diameter is 10–50nm is desirable.

[0047] As for the above-mentioned opening layer, it is desirable to have the binder, in order to maintain the property as a coat. Although various, conventionally well-known binders can be used as this binder, the hydrophilic binder with which the higher permeability of ink is acquired is used preferably. However, it is important for a binder to swell and not to take up an opening substantially in the activity of a hydrophilic binder, at the time of the osmosis in early stages of ink, and a hydrophilic binder with low bloating tendency is comparatively desirable near a room temperature from this viewpoint. Especially a desirable hydrophilic binder is the polyvinyl alcohol or cation conversion polyvinyl alcohol of perfect or a partial saponification.

[0048] one especially desirable also in polyvinyl alcohol — whenever [ saponification ] — 80 or more parts — or a full saponification is carried out. moreover, the viewpoint which improves coat

brittleness to average degree of polymerization — 500–3000 — the thing of 1000–3000 is used especially preferably.

[0049] Moreover, it is polyvinyl alcohol which has the 1–3rd class amino group which is indicated by JP,61–10483,A, for example, and the 4th class ammonium in the principal chain of the above-mentioned polyvinyl alcohol, or a side chain as cation conversion polyvinyl alcohol.

[0050] Moreover, although other hydrophilic binders can be made to contain in said opening layer, as for these hydrophilic-properties binder, it is desirable preferably that it is 20 or less % of the weight in general to the above-mentioned polyvinyl alcohol or cation conversion polyvinyl alcohol.

[0051] As for especially a volume ratio [ as opposed to the hydrophilic binder of a solid-state particle the case of the opening creation by the aforementioned \*\* or \*\* which is a desirable mode ] especially, in this invention, carrying out to five or more is [ three or more ] desirable. However, the volume said by this invention is the bulking value which broke weight by true specific gravity and found it, and it is unrelated to the volume of appearance including the opening inside a particle.

[0052] Moreover, although it is desirable to contain various kinds of oil droplets in order to improve the brittleness of a coat in this case, the solubility over the water in a room temperature can make about 0.01 or less % of the weight of hydrophobic high-boiling point organic solvents (a liquid paraffin, dioctyl phthalate, tricresyl phosphate, silicone oil, etc.) and a polymer particle (particle to which the one or more sort polymerization of the polymerization nature monomers, such as styrene, butyl acrylate, a divinylbenzene, butyl methacrylate, and hydroxyl ethyl methacrylate, was carried out) contain as such an oil droplet. Such an oil droplet can be preferably used ten to 50% of the weight to a hydrophilic binder.

[0053] As for the ink jet record form used for this invention which may differ as long as it is within the limits which the opening layer may consist of more than two-layer, and mentioned the configuration of those opening layers above in this case, it is desirable that the furthest maximum upper layer from a base material is an opening layer. This is because the advantage of an opening layer with quick absorption of ink can be efficiently employed in the maximum.

[0054] As a binder preferably used for the mordant content layer of an ink jet record form Gelatin or a gelatin derivative, a polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), A pullulan, polyvinyl alcohol, or its derivative (about 20,000 or more have desirable average molecular weight), A polyethylene glycol (100,000 or more have a desirable mean molecular weight), a carboxymethyl cellulose, Hydroxyethyl cellulose, a dextran, a dextrin, polyacrylic acid, and its salt, An agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, A polyalkylene oxide system copolymerization nature polymer given in locust bean gum, an alginic acid, gum arabic, a pullulan, JP,7–195826,A, and 7–9757, Polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has the carboxyl group and sulfonic group of a publication, can be mentioned to a water-soluble polyvinyl butyral or JP,62–245260,A. These hydrophilic binders may be used independently and may use two or more sorts together.

[0055] It is desirable that at least one sort uses reversibly a part of hydrophilic binder in which sol gel transformation is possible from a viewpoint of stability high-speed spreading, for example, it is desirable to use at least one sort of gelatin, a gelatin derivative, and a kappa carrageenan.

[0056] Moreover, acid-treatment gelatin is mentioned to moisture-proof and a water resisting property as a more effective binder. Generally, compatibility with a mordant is also well good and that of acid-treatment gelatin is desirable also from the point.

[0057] As for the binder of a mordant content layer, it is desirable that the dura mater is carried out. By this, the water resisting property to a lot of water can be raised more. When a binder is a non-dura mater, the binder swollen in the upper opening layer at the time of ink absorption invades, and there is an inclination to reduce ink absorptivity, by taking up an opening.

[0058] For example, when gelatin is chosen as a binder, hardening agents, such as chromium alum, formaldehyde, glyoxal, an epoxy system compound, a vinyl sulfone system compound, an acryloyl system compound, s-triazine system compound, N-methylol system compound, a carbodiimide system compound, and ethylene imino \*\*\*\*\*, are common knowledge. Moreover, when polyvinyl alcohol is chosen as a binder, hardening agents, such as borax, boric acid, borate, resorcinol, a



catechol, a phloroglucinol, a gallic acid, vanadium acid, oxalic acid, and N-methylol, are known.  
 [0059] As a mordant to the water soluble dye used by this invention Polyethyleneimine, JP,57-36692,A, 59-20696, 59-33176, 59-33177, 59-96987, No. 155088 [ 59 to ], 60-11389, 60-49990, 60-83882, 60-109894, 61-277484, 61-293886, 62-19483, 62-198493, 63-49478, 63-115780, 63-203896, 63-274583, 63-280681, 63-260477, The polymer or compound which has the amino group of the 1-3rd class or the 4th class ammonium indicated by JP,1-9776,A, 1-24784, 1-40371, 3-133686, 6-234268, 7-125411, etc. is used preferably.

[0060] It is desirable that light-fast degradation, small moreover, uses the basic latex polymer which has the 3rd class amino group or the 4th class ammonium among these comparatively as a mordant which has firm color mordancy.

[0061] The basic latex polymer which has the 3rd class or the 4th class nitrogen atom preferably used for this invention is expressed with the following general formula (L).

[0062]

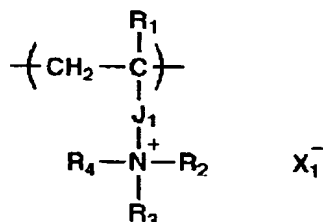
A general formula (L) A expresses the repeating unit guided from the monomer which has the 3rd class amino group or the 4th class ammonium, and which can be copolymerized among a (A)<sub>x</sub>-(B)<sub>y</sub>-(C)<sub>z</sub> type, B expresses the repeating unit guided from the monomer which has at least two ethylene nature partial-saturation radicals, and which can be copolymerized, and C expresses the repeating unit guided from the monomer which has ethylene nature partial-saturation radicals other than A and B at least, which can be copolymerized. x is [ z of y ] 0-90-mol % 0-10-mol% 10-98-mol%.

[0063] a general formula (L) — setting — A — especially — desirable — the following general formula (LA-1), (LA-2), and (LA-3) — or (LA-4) (LA-5) it is expressed.

[0064]

[Formula 1]

一般式(LA-1)

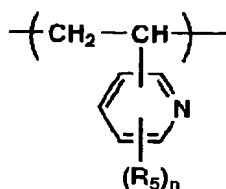


[0065] R1 expresses the alkyl group of a hydrogen atom or the carbon atomic numbers 1-4 among a formula. J1 expresses a divalent connection radical and expresses the benzyl which is not permuted [ a permutation or ] or -COY-. A carbon atomic number is the divalent connection radical of 1-20, for example, Y expresses an alkylene group, an arylene radical, a -O-Y'-radical, and a -NH-Y'-radical (Y' is an alkylene group, an arylene radical, an aralkylene group, etc.). R2, R3, and R4 may express the alkyl group of the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18 respectively, and these alkyl groups or an aralkyl radical may have a substituent. X1- expresses an anion, for example, expresses halogen ion, alkyl sulfonic-acid ion, aryl sulfonic-acid ion, acetic-acid ion, etc.

[0066]

[Formula 2]

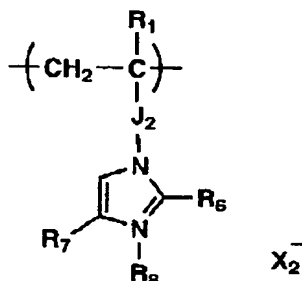
一般式(LA-2)



[0067] R5 expresses among a formula the alkyl group which has a hydrogen atom, an alkyl group, an

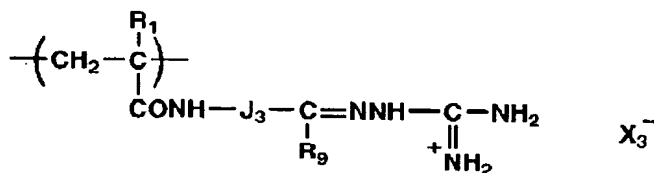
[0068]

### 一般式(LA-3)

$$\left( \text{CH}_2 - \overset{\overset{\text{R}_1}{|}}{\underset{\underset{\text{J}_2}{|}}{\text{C}}} \right) - \text{Imidazole}(\text{R}_6, \text{R}_7)$$


[0070]

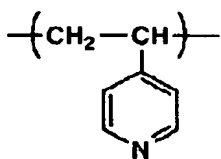
### 一般式(LA-5)



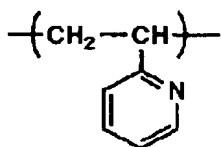
[0073]

[Formula 5]

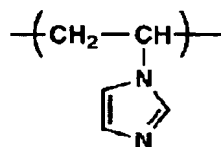
M-1



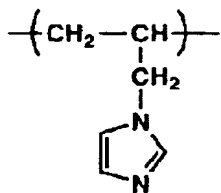
M-2



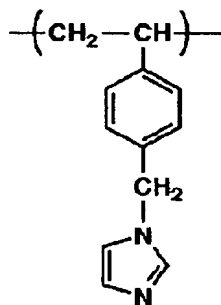
M-3



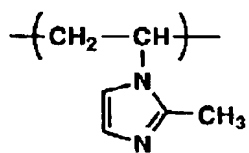
M-4



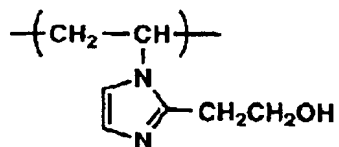
M-5



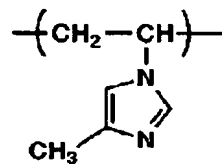
M-6



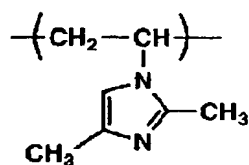
M-7



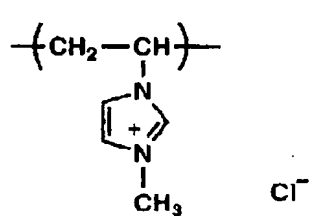
M-8



M-9

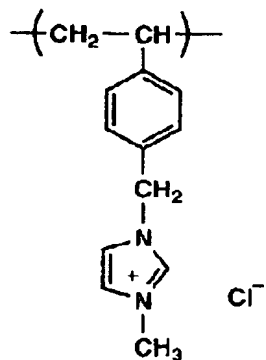


M-10

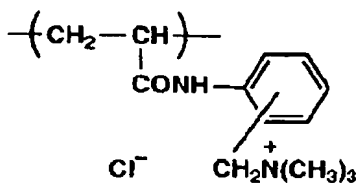


[0074]  
[Formula 6]

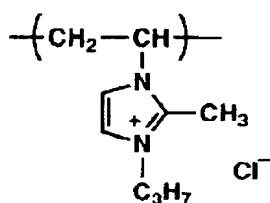
M-11



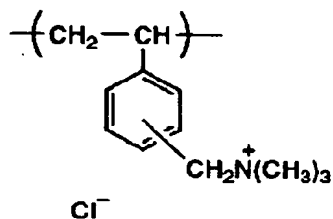
M-15



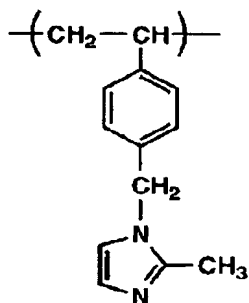
M-12



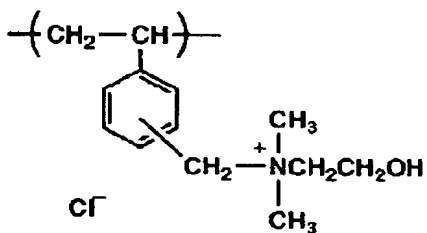
M-16



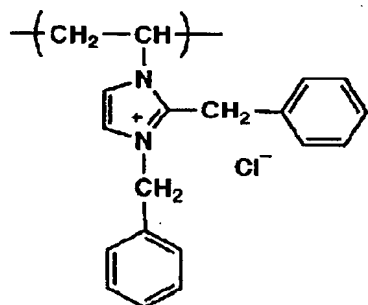
M-13



M-17



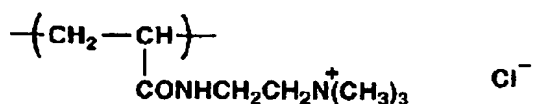
M-14



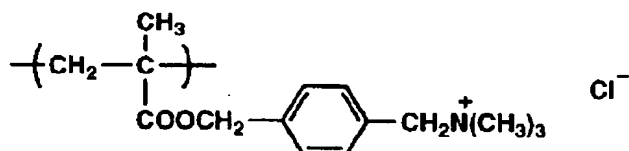
[0075]

[Formula 7]

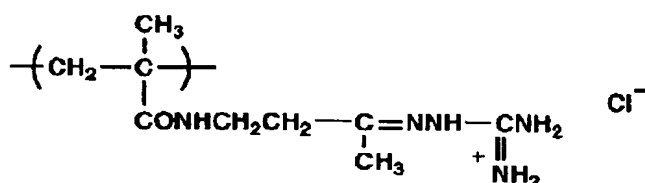
M-18



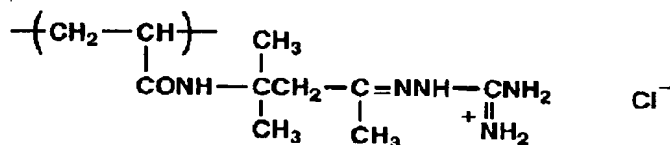
M-19



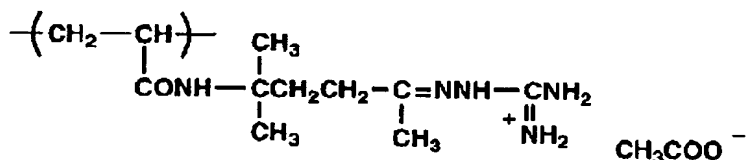
M-20



M-21



M-22



[0076] In a general formula (L), a divinylbenzene, ethylene glycol dimethacrylate, trimethylolpropane triacrylate, tetramethylene glycol diacrylate, propylene glycol dimethacrylate, etc. are mentioned as an example of the monomer which forms the repeating unit expressed with B. Moreover, as an example of the monomer which forms the repeating unit expressed with C, ethylene, 1-butene, styrene, an acrylic acid, a methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl acrylate, t-butyl acrylate, octyl acrylate, benzyl acrylate, acrylic nitril, a maleic acid, vinyl acetate, acrylamide, hydroxymethyl methacrylate, etc. are mentioned.

[0077] The example of a basic latex expressed with a general formula (L) is shown below. However, the monomer showed A, B, and C in a table, respectively.

[0078]

[A table 1]

番号	A	B	C	x	y	z
L-1	M-1	—	C-2	70	0	25
			C-5			5
L-2	M-3	B-1	C-2	70	4	26
L-3	M-5	B-1	C-2	70	4	26
L-4	M-3	B-1	C-4	76	4	20
L-5	M-3	B-1	C-1	70	4	26
L-6	M-5	B-1	C-1	70	4	26
L-7	M-5	B-2	C-1	70	4	26
L-8	M-3	B-1	C-1	40	4	26
	M-12			30		
L-9	M-5	B-1	C-7	70	4	26
L-10	M-5	B-1	C-1	60	2	20
			C-5			18
L-11	M-11	B-1	C-2	70	4	26
L-12	M-15	—	C-2	60	—	40
L-13	M-15	B-1	C-2	60	2	38

[0079]

[A table 2]

番号	A	B	C	x	y	z
L-14	M-15	—	C-6	65	—	35
L-15	M-16	—	C-2	75	—	25
L-16	M-18	B-1	C-1	70	4	26
L-17	M-16	B-1	C-1	70	4	16
			C-4			10
L-18	M-18	B-1	C-1	70	3	15
			C-4			12
L-19	M-18	B-1	C-1	65	4	19
			C-5			12
L-20	M-18	B-1	C-3	60	4	36
L-21	M-21	—	C-6	60	—	40
L-22	M-21	B-1	C-4	60	2	38
L-23	M-22	—	C-8	60	—	40
L-24	M-22	—	C-4	60	—	40
L-25	M-22	—	C-6	60	—	40
L-26	M-22	B-1	C-8	60	—	40

[0080] B-1 to B-2 in a table and C-1 to C-8 show the following.

[0081] B-1: Divinylbenzene B-2 : acrylamide C-7:N-vinyl-pyrrolidone C-8:N- ethylene glycol dimethacrylate C-1: — styrene — C-2:butyl acrylate C-3:t-butyl acrylate — C-4:vinyl acetate C-5:hydroxy MECHICHIRU methacrylate C-6 — (2-acetyl - 1, 1, - dimethyl ethyl) the amount of the mordant used in acrylamide this invention — 1m of record forms — 0.2-5g 0.1-10g per two is the range of 0.5-3g especially preferably preferably.

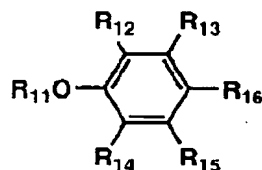
[0082] As for the ink jet record form used for this invention, it is desirable to make an image stabilizer contain in order to raise the lightfastness of water soluble dye. A water-soluble thing may be chosen and you may mix to coating liquid, and an image stabilizer may carry out oil distribution of the oil solubility thing, may make it an oil droplet, and may be mixed to coating liquid.

[0083] As a desirable image stabilizer, a general formula (ST-I) and (ST-II) the compound expressed are mentioned.

[0084]

[Formula 8]

一般式(ST-I)



[0085] R11 expresses a hydrogen atom, an alkyl group, an alkenyl radical, or an aryl group among a formula, and R12, R13, R14, R15, and R16 express a hydrogen atom, a halogen atom, a cyano group, a nitro group, hydroxyl, a sulfonic group, or a univalent organic radical respectively.

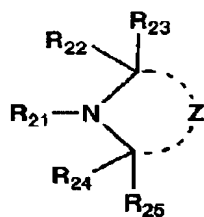
[0086] However, when R11 is a hydrogen atom, R12 and R14 are not hydrogen atoms simultaneously. Moreover, when R11 is an alkyl group, an alkenyl radical, or an aryl group, as for at least one of R12, R13, R14, R15, and the R16,  $-OR_{17}$  (R17 is an alkyl group or an alkenyl radical) or  $-N(R_{28})R_{29}$  (R28, and R29 are hydrogen atom, alkyl group, or alkenyl radical) respectively.

[0087] Respectively, it may join together mutually and R11, R12 and R12, R13 and R13, R16 and R16, R15 and R15, and R14, R14 and R11 may form a ring.

[0088]

[Formula 9]

一般式(ST-II)



[0089] R21 expresses a hydrogen atom, an alkyl group, an alkenyl radical, a phenyl group, hydroxyl, a sulfonyl group, a sulfinyl group, or an acyl group among a formula, and R22, R23, R24, and R25 express a hydrogen atom or an alkyl group respectively. Z expresses a nonmetal atom group required to form the nitrogen-containing heterocycle of 5 – 7 member.

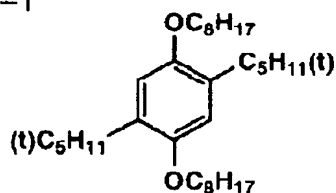
[0090] Respectively, it may join together mutually and R21, R22 and R22, R23 and R24, and R25, R24 and R21 may form a ring.

[0091] The example of the especially desirable image stabilizer used for this invention is shown below.

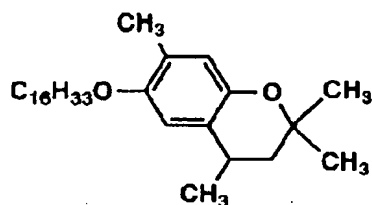
[0092]

[Formula 10]

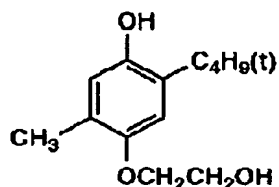
ST-1



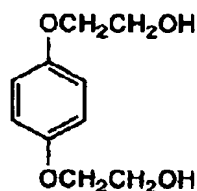
ST-2



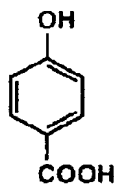
ST-3



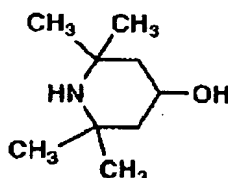
ST-4



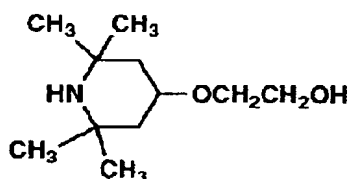
ST-5



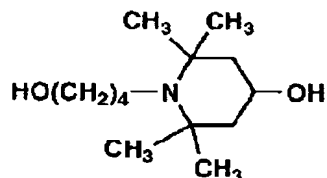
ST-6



ST-7



ST-8



[0093] An ink jet record form can make the compound which absorbs ultraviolet rays in order to raise the lightfastness of water soluble dye contain. As a compound which absorbs ultraviolet rays, the ultraviolet ray absorbent of a publication is mentioned, for example to JP,57-74193,A, 57-87988, 62-261476, etc. In order to make it ultraviolet rays not reach the water soluble dye which exists in a mordant layer, it is effective to see these ultraviolet ray absorbents from a base material rather than a mordant layer, and to make a far layer contain.

[0094] Further various kinds of additives can be made to contain if needed in the layer of the arbitration by the side of the ink receptiveness layer of an ink jet record form. For example, well-known additives, such as lubricant, such as pH regulators, such as the fluorescent brightener indicated by an anion, a cation or the various surfactants of Nonion, JP,59-42993,A, 59-52689, 62-280069, 61-242871, JP,4-219266,A, etc., a sulfuric acid, phosphoric acid, citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, and a diethylene glycol, antiseptics, a thickener, a hardening agent, an antistatic agent, and a mat agent, can also be



made to contain.

[0095] Although especially a limit does not have the amount of the spreading solid content by the side of the ink recording surface in an ink jet record form, 5 – 60 g/m<sup>2</sup> is desirable in general, and 10 – 40 g/m<sup>2</sup> is more desirable. in addition, \*\*\*\* which consists of the field of the curl prevention after record image formation — forming thinly is desirable.

[0096] As a base material of an ink jet record form, the base material which does not absorb water at all substantially among things well-known as a record form for ink jets can be used suitably conventionally.

[0097] The thing of a property which bears the radiant heat when the film which consists of ingredients, such as polyester system resin, diacetate system resin, triacetate system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, being mentioned as a transparence base material, and being used as an OHP also in this is desirable, and especially polyethylene terephthalate (PET) is desirable. As thickness of a transparence base material, about 10–200 micrometers is desirable. It is desirable from an adhesive viewpoint of an ink absorbing layer, a back layer, and a base material to prepare a well-known undercoating layer in an ink absorbing layer [ of a base material ] and back layer side.

[0098] Moreover, the so-called White pet which adds white pigments to the resin coat paper (the so-called RC paper) and PET which have the polyolefin resin enveloping layer which added white pigments etc., and grows at least into one side of a base paper as an opaque base material at them is desirable.

[0099] The approach of applying a hydrophilic layer on a base material can be suitably chosen from a well-known approach, and can be performed. On a base material, a desirable approach paints and dries the coating liquid containing the hydrophilic binder in which sol gel transformation like gelatin is possible, and obtains it. A hydrophilic binder layer has desirable simultaneous spreading which may exist more than two-layer, can also apply more than two-layer simultaneously in this case, and substitutes all hydrophilic binder layers for one spreading especially.

[0100] For example, after cooling and making into the gel state hydrophilic binder content ink absorbing layers in which sol gel transformation is possible, such as gelatin which is indicated by JP,6–64306,A, after applying on a base material, the approach of drying by the cold dry cleaning method is one of the desirable approaches.

[0101] The extrusion coat method which uses the hopper of a publication for the roll coating method, a rod bar coating method, the air-knife-coating method, a spray coating method, the curtain applying method, or a U.S. Pat. No. 2,681,294 number as a spreading method is used preferably.

[0102] the ink jet recording method in which the regurgitation [ water-soluble ink ] of the regurgitation method of the ink used for the ink jet record approach is possible — it is — \*\*\*\*\* — for example, Koichi Nakamura editing — recording methods, such as a continuation injection electrification control system, a method on demand, etc. of a publication, can be used for work “trend of ink jet record technique” (Japanese science-information company \*\*, 1995) 1–14 page. Bigger effectiveness can be acquired by using it also in these, applying to the recording method of a method on demand.

[0103] Water-soluble ink is ink which contains water soluble dye as main sources of coloring, and contains water and a hydrophilic solvent.

[0104] The ink maximum delivery in this invention is the maximum of the amount of ink volume per [ which can be used when the ink jet printer used for this invention outputs all the usual images ] unit area. For example, it is not necessarily the ink maximum delivery which added the amount of ink for obtaining the maximum density of yellow, Magenta, cyanogen, and black each monochrome in the case of the printer for color pictures.

[0105] An ink maximum delivery can be calculated by count, if the volume of one drop of liquid ink drop is known and the array approach of the drop for forming an image is known.

[0106]

[Example] Although the example of this invention is given and explained below, this invention is not limited to these. In addition, “%” in an example shows oven-dry-weight %, as long as there is no notice especially, and an addition shows the amount per two 1m of ink jet record forms.

[0107] the paper base material (the inside of the polyethylene layer by the side of 140 micrometers in thickness, and a recording surface — 7% of the weight of anatase mold titanium-dioxide content — carrying out — the rear-face side of a recording surface — as a back layer) which covered 100g/stencil both sides of m<sup>2</sup> with polyethylene It multilayer-simultaneous-applied and the coating liquid of the presentation shown in tables 3, 4, 5, and 6 at a recording surface side, respectively in [ having a layer containing alkali treatment gelatin 1.2 g/m<sup>2</sup> and a hardening agent ] was dried, it adjusted so that it might become the desiccation thickness and void volume in a table, and the record forms 1-11 were obtained.

[0108] In addition, the void volume in a record form was calculated as follows. That is, the cross section of a sample is observed with an optical microscope, an electron microscope, etc., and the thickness of an ink absorbing layer is measured. Since the volume of solid content can be known from the presentation of this ink absorbing layer, the thickness when presupposing that the opening is not made is calculable. Since the difference of this measured value and calculated value is the thickness which increased by the opening, that void volume can be known by count.

[0109]

[A table 3]

記録用紙 1			
上層	純水	790ml	乾燥膜厚 0.5 $\mu\text{m}$
	P Cゼラチン (アミノ基封鎖率: 約88%)	40 g	
	P V A	25 g	
	界面活性剤- 1	0.7 g	
	界面活性剤- 2	0.3 g	
中層	純水	500ml	空隙容量 20ml / m <sup>2</sup>
	炭酸カルシウム (平均粒径: 約0.07 $\mu\text{m}$ )	192 g	
	P V A (鹸化度: 89%, 平均重合度: 2,350)	12.8 g	
	界面活性剤- 3	1.2 g	
下層	純水	790ml	乾燥膜厚 2.0 $\mu\text{m}$
	P Cゼラチン (アミノ基封鎖率: 約88%)	40 g	
	P V A	25 g	
	媒染剤- 1	10 g	
	界面活性剤- 1	0.7 g	
	界面活性剤- 2	0.3 g	

記録用紙 2			
上層	純水	790ml	乾燥膜厚 0.5 $\mu\text{m}$
	P Cゼラチン (アミノ基封鎖率: 約88%)	40 g	
	P V A	25 g	
	界面活性剤- 1	0.7 g	
	界面活性剤- 2	0.3 g	
中層	純水	980ml	空隙容量 20ml / m <sup>2</sup>
	微粒子シリカ (平均粒径: 約0.07 $\mu\text{m}$ )	48.2 g	
	P V A (鹸化度: 89%, 平均重合度: 2,350)	12.8 g	
	界面活性剤- 3	1.2 g	
下層	純水	790ml	乾燥膜厚 2.0 $\mu\text{m}$
	P Cゼラチン (アミノ基封鎖率: 約88%)	40 g	
	P V A	25 g	
	媒染剤- 1	10 g	
	界面活性剤- 1	0.7 g	
	界面活性剤- 2	0.3 g	

P Cゼラチン: フェニルカルバモイル化ゼラチン

P V A: ポリビニルアルコール

[0110]

[A table 4]

記録用紙 3			
上層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤-1 界面活性剤-1 界面活性剤-2	790ml 40g 25g 10g 0.7g 0.3g	乾燥膜厚 2.0 $\mu\text{m}$
下層	純水 微粒子シリカ（平均粒径：約0.07 $\mu\text{m}$ ） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2g 12.8g 1.2g	空隙容量 20ml/ $\text{m}^2$
記録用紙 4			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu\text{m}$ ） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2g 12.8g 1.2g	空隙容量 20ml/ $\text{m}^2$
下層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤-1 界面活性剤-1 界面活性剤-2	790ml 40g 25g 10g 0.7g 0.3g	乾燥膜厚 2.0 $\mu\text{m}$
記録用紙 5			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu\text{m}$ ） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2g 12.8g 1.2g	空隙容量 20ml/ $\text{m}^2$
下層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤-1 界面活性剤-1 界面活性剤-2	790ml 40g 25g 10g 0.7g 0.3g	乾燥膜厚 2.0 $\mu\text{m}$

[0111]

[A table 5]

記録用紙 6			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu\text{m}$ ） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤－3	930ml 140 g 12.8 g 1.2 g	空隙容量 20ml/ $\text{m}^2$
下層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤－1 界面活性剤－1 界面活性剤－2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu\text{m}$
記録用紙 7			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu\text{m}$ ） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤－3	980ml 48.2 g 12.8 g 1.2 g	空隙容量 20ml/ $\text{m}^2$
下層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤－2 界面活性剤－1 界面活性剤－2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu\text{m}$
記録用紙 8			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu\text{m}$ ） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤－3	980ml 48.2 g 12.8 g 1.2 g	空隙容量 20ml/ $\text{m}^2$
下層	純水 酸処理ゼラチン PVA 媒染剤－1 界面活性剤－1 界面活性剤－2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu\text{m}$

[0112]

[A table 6]

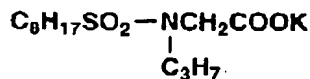
記録用紙9			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2g 12.8g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 酸処理ゼラチン PVA 媒染剤-1 硬膜剤-1 界面活性剤-1 界面活性剤-2	790ml 40g 25g 10g 2g 0.7g 0.3g	乾燥膜厚 2.0 $\mu$ m
記録用紙10			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2g 12.8g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 酸処理ゼラチン PVA 媒染剤-1 画像安定剤（例示ST-5） 硬膜剤-1 界面活性剤-1 界面活性剤-2	780ml 40g 25g 10g 10g 2g 0.7g 0.3g	乾燥膜厚 2.0 $\mu$ m
記録用紙11			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 分散物-1 界面活性剤-3	980ml 48.2g 12.8g 5g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 酸処理ゼラチン PVA 媒染剤-1 硬膜剤-1 界面活性剤-1 界面活性剤-2	780ml 40g 25g 10g 2g 0.7g 0.3g	乾燥膜厚 2.0 $\mu$ m

[0113] The structure of the raw material used for record form production is as follows.

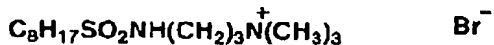
[0114]

[Formula 11]

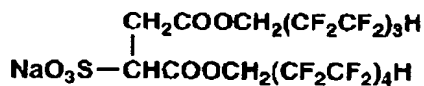
### 界面活性剤-1



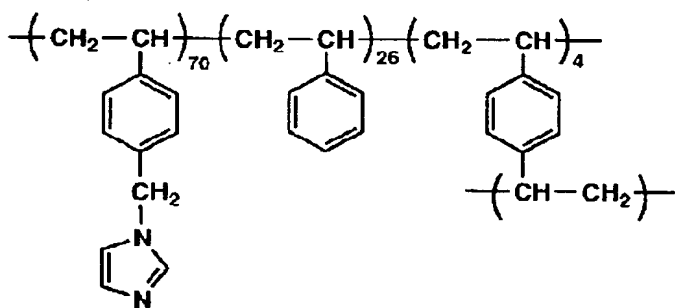
### 界面活性剤-2



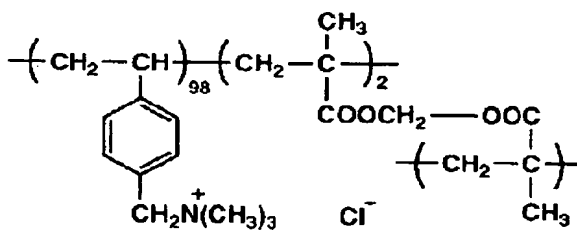
### 界面活性剂-3



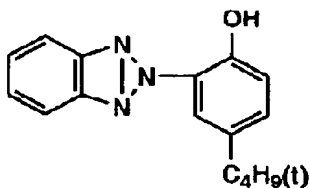
### 媒染剂-1



## 媒染剂-2



### 紫外線吸収剤-1



**[0115] (Distributed object -1) The solution 1 and solution 2 of the following presentation were prepared, and it mixed, and distributed in the ultrasonic disperser.**

[0116] Solution 1 ultraviolet ray absorbent -1 1g G i-DESHIRU phthalate 1g ethyl acetate 5ml solution 2PC gelatin (thing given in a table) 0.5g surfactant -4 0.2g pure water 15ml surfactant -4: To the record forms 1-11 of the tree i-propyl naphthalene sulfonic-acid sodium above, it is a line with a monochrome solid [ of a Magenta ], and a width of face of 1mm with an ink jet printer on demand. It printed. Printing environments are the room temperature of 23 degrees C, and 50% of relative humidity, and ink discharge quantity is 21 ml/m2.

[0117] The following items estimated to the obtained pattern and the result shown in a table 7 was obtained.

[0118] The sample of the maximum-density part of a << lightfastness >> Magenta was asked for

the ratio of the reflection density before 24-hour Mitsuteru putting, and an exposure after an exposure in xenon fade meter.

[0119] The << water resisting property >> printing sample was dried after being immersed for 10 minutes into 20-degree C water, and residual concentration compared the water resisting property of the printing image of the maximum-density part of a Magenta color. O evaluated what has high concentration and the low thing was evaluated in four steps of x.

[0120] After saving the sample after << moisture resistance >> printing for two weeks at 23 degree C and 20% of relative humidity, it saved for three days at 60 degree C and 80% of relative humidity, and the blot degree of each color was investigated.

[0121] Assessment carried out the visual judgment of the flare of a line before and after saving at 60 degree C and 80% of relative humidity on the following criteria.

[0122]

O : blot-less O:blot width of face is completely less than (extent a blot is slightly accepted to be in feeling of \*\*) about 0.1mm.

\*\* : Blot width of face is 0.1mm - less than (allowance is impossible in feeling of \*\*) 0.5mm.

x : Blot width of face is 0.5mm or more (level which does not almost have the value as an image).

The visual judgment of the degree of the ink which the load of superposition and 100 g/cm<sup>2</sup> was applied, left the rear face of the same record form for 1 minute, and imprinted it at the rear face to the printing side after [ of an after / << drying >> printing ] 2 minutes was carried out on the following criteria.

[0123]

O : — completely — imprint-less O: — although there is an imprint faintly — a subject-copy image — almost — effect-less x: — a lot of ink imprinted, and the subject-copy image carried out 20-point density measurement of the solid section of a << concentration nonuniformity >> printing sample which does not bear admiration by the microdensitometer (the diameter of an aperture: 200 micrometers), and asked for the standard deviation of a concentration value.

[0124] [A table 7]

記録用紙No.	耐光性	耐水性	耐湿性	乾燥性	濃度ムラ
1 (本発明)	60	△	○	○	0.4
2 (本発明)	75	△	○	○	0.6
3 (比較例)	30	○	○	○	0.9
4 (比較例)	25	×	×	×	1.5
5 (本発明)	75	△	△	○	0.1
6 (本発明)	80	△	△	◎	0.0
7 (本発明)	75	△	○	○	0.1
8 (本発明)	70	○	○	○	0.1
9 (本発明)	70	◎	○	○	0.1
10 (本発明)	90	◎	○	○	0.1
11 (本発明)	95	◎	○	○	0.1

[0125]

[Effect of the Invention] It became possible from the above result to excel in light-proof, a deck watertight luminaire, and moisture resistance, and to offer a high-definition ink jet record image with little concentration nonuniformity by this invention.

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[Translation done.]

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the ink jet record form which has improved especially ink absorptivity about the ink jet record form which records using water soluble dye.

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## PRIOR ART

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[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, it is comparatively alike and a high speed, the low noise, and multiple-color-izing are easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread quickly in various fields, such as various printers, facsimile, and a computer terminal, in current.

[0003] As a record form used by this ink jet recording method, when a printing dot laps [ that the concentration of a printing dot is high and a color tone is brightly skillful, and absorption of ink ] early, ink flows out or it spreads, or the diffusion to the longitudinal direction of not carrying out and a printing dot is not large beyond the need, and for the circumference to be smooth and not to fade etc. is demanded.

[0004] When especially ink rate of absorption is slow, in case the liquid ink drop of two or more colors laps and is recorded, in order to become nonuniformity, and for a mutual color to spread in the border area of a color which a drop causes a HAJIKI phenomenon on a record form, and is different and to be easy to reduce image quality greatly, it is required to have ink absorptivity high as a record form.

[0005] In order to solve these problems, very many techniques are proposed from the former. As the pigment in the record form which carried out humidity of the coating for surface treatment to the low size stencil indicated by JP,52-53012,A, the record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, and the clad layer indicated by JP,56-157,A The record form containing non-colloid silica powder, the record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The record form which has two hole distribution peaks indicated by JP,58-110287,A, The record form which consists of the vertical two-layer porous layer indicated by JP,62-111782,A, The record form which has the infinite form crack indicated by JP,59-68292,A, 59-123696, 60-18383, etc., The record form which has the impalpable powder layer indicated by JP,61-135786,A, 61-148092, 62-149475, etc., JP,63-252779,A, JP,1-108083,A, 2-136279, The record form containing the pigment which has the specific physical-properties value indicated by 3-65376, 3-27976, etc., or a particle silica, JP,57-14091,A, 60-219083, 60-210984, 61-20797, 61-188183, JP,5-278324,A, 6-92011, 6-183134, 7-137431, The record form containing particle silicas, such as a colloid silica indicated by 7-276789 etc., A large number, such as a record form containing the hydrated alumina particle indicated by JP,2-276671,A, 3-67684, 3-215082, 3-251488, 4-67986, 4-263983, 5-16517, etc., are known.

[0006] However, since many ink absorbing layers with many openings will have irregularity with micro interface with air and coat front face, the incident light to an ink absorbing layer is scattered about or transparency is barred when an ink absorbing layer absorbs ink or it consists of only layers which have many openings for holding, it becomes or tends to be hard to come out opaquely lusterless.

[0007] Moreover, in order to form an opening, there is a fault out of which the smooth nature on the front face of a coat by own irregularity of a pigment or the irregularity of the secondary floc of

a pigment falls, and gloss cannot come easily.

[0008] On the other hand, many ink jet record forms of the type which absorbs ink and is held in a swelling operation of the binder of an ink absorption layer are also known, without preparing an opening into a coat. For example, many the recording papers, films, etc. which applied hydrophilic binders, such as gelatin, casein, starch, an alginic acid, polyvinyl alcohol, various kinds of conversion polyvinyl alcohol, a polyvinyl pyrrolidone, polyethylene oxide, polypropylene oxide, a carboxymethyl cellulose, HIDOROKI ethyl cellulose, a dextran, and a pullulan, on the base material as binders are known from the former.

[0009] Although these record forms are inferior in ink absorptivity compared with the record form which has the above-mentioned opening, high glossiness and optical density, and a clear image are obtained, and they are useful as a high-definition record application.

[0010] The ink jet record form which carried out the laminating of the upper layer which changes from hydrophilic resin, a non-subtlety particle, and a bulking agent to the lower layer which changes from water soluble resin to JP,7-186521,A as what combined the above two types is indicated. Moreover, as it is in JP,61-12388,A, 61-35275, 61-49883, 61-49884, 61-49885, 61-135787, 61-135788, 62-196175, 62-222887, etc., the ink jet record form which prepared the ink transparency layer in the upper layer rather than the ink maintenance layer is known.

[0011] since a coloring matter molecule existed between the inside of a binder, and an opening independently unlike the color photographic paper in which a coloring matter molecule be distribute in the state of a high-concentration particle in oils, a fault which waterdrop be pour on a recording surface, or coloring matter spread when it be save under high humidity conditions the printing back for a long period of time, or be easy flow out be in various kinds of ink jet record forms suitable for the water-soluble above-mentioned ink.

[0012] In order to improve the water resisting property and moisture resistance of this coloring matter, the various methods of making coloring matter fix in a binder from the former are proposed. Especially an effective means is the approach of adding as a particle latex by using as a uniform water solution the polymer which has the nitrogen atom of the 3rd class or the 4th class.

[0013] For example, the ink jet record form applied on the stencil or the polyethylene terephthalate (PET) film base material by using as an ink absorbing layer the coating liquid which contains a basic mordant for gelatin as some binders is indicated by JP,57-36692,A.

[0014] Moreover, the water-color-ink record form which made JP,53-49113,A carry out impregnation of the polyethyleneimine into paper; in JP,58-24492,A The record ingredient which has the electrolyte polymer which has a cation or an anion radical; to JP,63-224988,A The charge of a recorded material which contains the 1st class - tertiary amine, or quarternary ammonium salt in an ink absorbing layer, and has pH of an ink maintenance layer in 2-8; to JP,63-307979,A The ink jet record sheet which has a layer containing the hydrophilic polymer mordant which has the 3rd class or the 4th class nitrogen atom, and the polymer which has a hydrophilic radical; to JP,59-198186,A and 59-198188 The charge of a recorded material which made the organic base of polyethyleneimine contain in the coating layer in a base material or on a base material; to JP,60-46288,A The ink jet record approach using the ink containing a specific color, and the record ingredient containing polyamine etc.; JP,61-61887,A, To 61-72581, 61-252189, and 62-174184 The ink jet record form containing the poly allylamine; to JP,61-172786,A the polymer which has an intermolecular hydrogen bridge, and the polymer (a polyethylene glycol —) which does not have a hydrogen bond nature machine among molecules (gelatin, polyethyleneimine, etc.) The ink jet record ingredient containing a polyvinyl pyrrolidone etc.; to JP,63-162275,A A cationic polymer and a cationic surface active agent on a base material to spreading or ink jet record form; JP,6-143798,A which carried out impregnation The record sheet which superimposed the color fixation layer which uses a quarternary-ammonium-salt polymerization object and cation conversion polyvinyl alcohol as a principal component on a plastics base material, and the color transparency and ink absorption layer which were prepared on it is indicated.

[0015] Generally it is [ causing thickening and condensation in many cases ] difficult during preparation / spreading to include a polymer with such color fixing ability in an opening layer. Moreover, even if it incorporates, in order that a color may fix in an opening layer, there is an inclination for a color to be exposed to the oxygen in air and to degrade lightfastness. It was rare

to include a polymer with color fixing ability in an opening layer conventionally from these reasons. [0016] It is possible to, incorporate the polymer which has the above-mentioned color fixing ability comparatively easily about the ink jet record form of the type which absorbs ink and is held in a swelling operation of the binder of an ink absorption layer, without preparing an opening into a coat on the other hand. However, it is a problem as above-mentioned that the layer which consists of this type of water-soluble binder has the late absorptivity of ink.

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**EFFECT OF THE INVENTION**

---

[Effect of the Invention] It became possible from the above result to excel in light-proof, a deck watertight luminaire, and moisture resistance, and to offer a high-definition ink jet record image with little concentration nonuniformity by this invention.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] The object of this invention is in the improvement of an ink jet record form which used water soluble dye, the high definition record by absorption of quick ink is possible, the water resisting property and moisture resistance of a color after record are improved [ this invention is made in view of the above-mentioned actual condition, ], and it is in offering the ink jet record form in which lightfastness moreover is not reduced.

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## MEANS

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[Means for Solving the Problem] The object of above-mentioned this invention is attained by the following configurations.

[0019] (1) The ink jet record form which has the opening layer prepared at the side which is separated from a base material from the mordant content layer and this mordant content layer which fix water soluble dye on the base material which does not absorb water at all substantially, and an ink maximum delivery has [ the void volume of this opening layer ] 90% or more.

[0020] (2) An ink jet record form given in (1) whose furthest layer from a base material is an opening layer.

[0021] (3) (1) to which the dura mater of the binder of a mordant content layer is carried out, or an ink jet record form given in (2).

[0022] (4) (1) whose a mordant is a tertiary amine system polymer or a quaternary-ammonium-salt system polymer, (2), or an ink jet record form given in (3).

[0023] (5) An ink jet record form given in (4) which contains acid-treatment gelatin in a mordant content layer.

[0024] (6) (4) which contains an image stabilizer in a mordant content layer, or an ink jet record form given in (5).

[0025] (7) (4) containing the compound which absorbs ultraviolet rays in the layer which is in a far side rather than a mordant content layer to a base material, (5), or an ink jet record form given in (6).

[0026] (8) An ink jet record form given in any 1 term of (1) - (7) the non-subtlety particle in an opening layer and whose volume ratio of a binder are five or more.

[0027] (9) The opening layer made the inorganic solid-state particle condense at the time of coating liquid preparation or coat formation, made the three-dimensional structure form, and was obtained, and it is an ink jet record form given in any 1 term of (1) - (8).

[0028] Hereafter, this invention is explained more to a detail.

[0029] The opening layer which the ink jet record form used for this invention has consists of the opening formed solid-state components, such as a hydrophilic property or a hydrophobic binder, an inorganic or organic particle, or an oil droplet, and between them.

[0030] It is common that the solid-state components which can perform formation of an opening by various methods and an opening layer contains by the approach also differ. The formation approach of a typical opening layer is explained below.

[0031] The uniform coating liquid containing two or more sorts of polymers is applied on a base material. \*\* In a desiccation process The coating liquid containing the approach \*\* solid-state particle and hydrophilic property, or hydrophobic binder which is made to carry out phase separation of these polymers mutually, and forms an opening is immersed in the liquid which contains water or a suitable organic solvent for a record form after spreading / desiccation at a base material top. In a desiccation process after applying the coating liquid containing the compound which has the property which foams at the time of the approach \*\* coat formation which is made to dissolve a solid-state particle and creates an opening The coating liquid containing the approach \*\* porosity solid-state particle and the hydrophilic binder which this compound is made to foam and form an opening into a coat is applied on a base material. As

opposed to the approach \*\* hydrophilic-property binder which forms an opening between the inside of a porosity particle, or a particle The coating liquid containing the solid-state particle and/or particle oil droplet which have the volume more than equivalent weight (preferably 1.0 or more times) in general, and a hydrophilic binder is applied on a base material. Between solid-state particles The approach the approach \*\* mean particle diameter which creates an opening makes solid-state particle about 0.1 micrometers or less condense at the time of coating liquid preparation or coat formation, forms a secondary particle or the three-dimensional structure, and creates an opening.

[0032] As for the opening formation approach in this invention, it is desirable to use the approach of not much not reducing the glossiness on the front face of the recording paper, with any above-mentioned means, although it is good. About 0.5 micrometers, the magnitude of an opening for that is about 0.2 micrometers or less, and it is preferably desirable to set up so that the magnitude of packing and the manufacture conditions at the time of coat formation may also turn into conditions which form such an opening especially preferably about 0.3 micrometers.

[0033] The approach of creating without taking a complicated production process from a viewpoint referred to as creating an ink jet record form by low cost on the other hand is desirable.

[0034] The desirable methods of hitting carrying out this invention from the above viewpoint are the above-mentioned \*\*, \*\*, and \*\*, and especially a desirable thing is the approach of \*\* or \*\*.

[0035] The total amount of the void volume of the opening layer of the ink jet record form used for this invention needs to be 90% or more of the maximum delivery of ink. Even when the layer containing a mordant is in the upper layer from an opening layer unlike this invention, and the void volume of an opening layer does not fulfill 90% of the maximum delivery of ink, the problem which ink overflows and worsens drying in the case of printing of the high amount of ink is not produced. However, only within the case where it is in the upper layer rather than the layer in which an opening layer contains a mordant, ink overflows in the case of printing of the high amount of ink, image quality is reduced or problems, like drying [ after printing ] is late arise.

[0036] Void volume is the value which deducted the total amount of the capacity of solid content, such as a binder in an opening layer, and various kinds of bulking agents, from the desiccation thickness in an opening layer, and voidage shows the rate of the amount of openings to the capacity of these solid content here.

[0037] It is good to carry out voidage preferably more than 250 capacity %. Although the upper limit of voidage generally changes with the class of bulking agent, or the classes of binder, generally it is below 400 capacity % from the reinforcement as a coat, brittleness, etc.

[0038] When there is an opening layer in the opening layer containing a solid-state particle, as a solid-state particle, a well-known solid-state particle inorganic [ various kinds of ] or organic can be conventionally used in an ink jet record form.

[0039] As an example of the above-mentioned inorganic particle, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, diatomaceous earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide, etc. can be mentioned. Such a non-subtlety particle may be added in the condition of having been used after homogeneity had distributed in the binder with the primary particle, and having formed secondary floc, and having distributed in the binder.

[0040] On the other hand, as an example of an organic particle, polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, melamine resin, etc. are mentioned.

[0041] In this invention, it is more desirable than the point of high concentration being attained, and a clear image being recorded and being able to manufacture by low cost to use the solid-state particle chosen from a hydrated alumina particle, a silica particle, and a calcium carbonate as a solid-state particle.

[0042] The alumina or hydrated alumina used preferably is the porosity alumina whose sum of the pore volume whose radius is 3-10nm is 0.2 - 2 cc/g, or its hydrated compound. The measurement

means of pore volume can be measured with a well-known nitrogen adsorption process to an alumina or the desiccation solid content of hydrated alumina.

[0043] An alumina or hydrated alumina may be crystalline, or may be amorphous, and a configuration can use the thing of the configuration of arbitration, such as an infinite form particle, a spherical particle, and a needlelike particle.

[0044] Silicas of the configuration of arbitration, such as a synthetic silica which could use various kinds of well-known silica system particles by the ink jet conventionally, for example, was compounded by wet or the gaseous-phase method as a silica system particle used for this invention, colloidal silica, and a porosity silica which a primary particle condenses and forms the secondary particle, can be used. As such an example, for example, the synthetic amorphous silica indicated by JP,55-51583,A, 56-148583, etc., The silica ultrafine particle compounded by the gaseous-phase method indicated by JP,60-204390,A, The synthetic infinite form silica containing the fluorine indicated by JP,60-222282,A, The synthetic infinite form silica in which surface treatment was carried out by the silane coupling agent indicated by JP,60-224580,A and 62-178384, The spherical silica indicated by JP,62-183382,A and 63-104878, The synthetic silica particle whose Na<sub>2</sub>O content indicated by JP,63-317381,A is 0.5 % of the weight or more, The specific surface area indicated by JP,1-115677,A The synthetic silica particle more than 100m<sup>2</sup>/g, The synthetic silica particle which was indicated by JP,62-286787,A and by which alumina surface treatment was carried out, The synthetic silica particle by which surface treatment was carried out by calcium and Mg which were indicated by JP,1-259982,A, or Ba, The colloidal silica oil absorption was indicated to be by 180cc[/g ] or more k composition silica particle and JP,57-14091,A, The cationic colloidal silica indicated by JP,60-219084,A, JP,6-92011,A, 6-297830, and 7-81214, Connection/or branched colloidal silica can be mentioned in the shape of [ which was indicated by JP,5-278324,A and 7-81214 ] a rosary.

[0045] However, in order to obtain high glossiness and high void volume, it is desirable to use the silica ultrafine particle whose mean particle diameter is 7-30nm. Cation conversion of the front face could be carried out, and this silica particle could be processed by aluminum, calcium, Mg, Ba, etc.

[0046] As a calcium carbonate used for the record form of this invention For example, JP,5712-486,A, 57-129778, 58-55283, The precipitated calcium carbonate which has specific surface area in the specification indicated by 61-20792, The needle pillar-shaped calcium carbonate indicated by JP,63-57277,A and JP,4-250091,A, The calcium-carbonate particle which the specific needlelike primary particle indicated by JP,3-251487,A condensed, and formed the secondary particle, the needle which has the specific oil absorption indicated by JP,4-250091,A and 4-260092 — a pillar-shaped prismatic crystal Argo night calcium carbonate, the spherical precipitated calcium carbonate indicated by JP,7-40648,A are mentioned. Since high glossiness and high void volume can be obtained, it is desirable that particle size uses calcium-carbonate particle about 0.1 micrometers or less, and the activity of the calcium-carbonate particle especially whose mean particle diameter is 10-50nm is desirable.

[0047] As for the above-mentioned opening layer, it is desirable to have the binder, in order to maintain the property as a coat. Although various, conventionally well-known binders can be used as this binder, the hydrophilic binder with which the higher permeability of ink is acquired is used preferably. However, it is important for a binder to swell and not to take up an opening substantially in the activity of a hydrophilic binder, at the time of the osmosis in early stages of ink, and a hydrophilic binder with low bloating tendency is comparatively desirable near a room temperature from this viewpoint. Especially a desirable hydrophilic binder is the polyvinyl alcohol or cation conversion polyvinyl alcohol of perfect or a partial saponification.

[0048] one especially desirable also in polyvinyl alcohol — whenever [ saponification ] — 80 or more parts — or a full saponification is carried out. moreover, the viewpoint which improves coat brittleness to average degree of polymerization — 500-3000 — the thing of 1000-3000 is used especially preferably.

[0049] Moreover, it is polyvinyl alcohol which has the 1-3rd class amino group which is indicated by JP,61-10483,A, for example, and the 4th class ammonium in the principal chain of the above-mentioned polyvinyl alcohol, or a side chain as cation conversion polyvinyl alcohol.



[0050] Moreover, although other hydrophilic binders can be made to contain in said opening layer, as for these hydrophilic-properties binder, it is desirable preferably that it is 20 or less % of the weight in general to the above-mentioned polyvinyl alcohol or cation conversion polyvinyl alcohol.

[0051] As for especially a volume ratio [ as opposed to the hydrophilic binder of a solid-state particle the case of the opening creation by the aforementioned \*\* or \*\* which is a desirable mode ] especially, in this invention, carrying out to five or more is [ three or more ] desirable. However, the volume said by this invention is the bulking value which broke weight by true specific gravity and found it, and it is unrelated to the volume of appearance including the opening inside a particle.

[0052] Moreover, although it is desirable to contain various kinds of oil droplets in order to improve the brittleness of a coat in this case, the solubility over the water in a room temperature can make about 0.01 or less % of the weight of hydrophobic high-boiling point organic solvents (a liquid paraffin, dioctyl phthalate, tricresyl phosphate, silicone oil, etc.) and a polymer particle (particle to which the one or more sort polymerization of the polymerization nature monomers, such as styrene, butyl acrylate, a divinylbenzene, butyl methacrylate, and hydroxyl ethyl methacrylate, was carried out) contain as such an oil droplet. Such an oil droplet can be preferably used ten to 50% of the weight to a hydrophilic binder.

[0053] As for the ink jet record form used for this invention which may differ as long as it is within the limits which the opening layer may consist of more than two-layer, and mentioned the configuration of those opening layers above in this case, it is desirable that the furthest maximum upper layer from a base material is an opening layer. This is because the advantage of an opening layer with quick absorption of ink can be efficiently employed in the maximum.

[0054] As a binder preferably used for the mordant content layer of an ink jet record form Gelatin or a gelatin derivative, a polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), A pullulan, polyvinyl alcohol, or its derivative (about 20,000 or more have desirable average molecular weight), A polyethylene glycol (100,000 or more have a desirable mean molecular weight), a carboxymethyl cellulose, Hydroxyethyl cellulose, a dextran, a dextrin, polyacrylic acid, and its salt, An agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, A polyalkylene oxide system copolymerization nature polymer given in locust bean gum, an alginic acid, gum arabic, a pullulan, JP,7-195826,A, and 7-9757, Polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has the carboxyl group and sulfonic group of a publication, can be mentioned to a water-soluble polyvinyl butyral or JP,62-245260,A. These hydrophilic binders may be used independently and may use two or more sorts together.

[0055] It is desirable that at least one sort uses reversibly a part of hydrophilic binder in which sol gel transformation is possible from a viewpoint of stability high-speed spreading, for example, it is desirable to use at least one sort of gelatin, a gelatin derivative, and a kappa carrageenan.

[0056] Moreover, acid-treatment gelatin is mentioned to moisture-proof and a water resisting property as a more effective binder. Generally, compatibility with a mordant is also well good and that of acid-treatment gelatin is desirable also from the point.

[0057] As for the binder of a mordant content layer, it is desirable that the dura mater is carried out. By this, the water resisting property to a lot of water can be raised more. When a binder is a non-dura mater, the binder swollen in the upper opening layer at the time of ink absorption invades, and there is an inclination to reduce ink absorptivity, by taking up an opening.

[0058] For example, when gelatin is chosen as a binder, hardening agents, such as chromium alum, formaldehyde, glyoxal, an epoxy system compound, a vinyl sulfone system compound, an acryloyl system compound, s-triazine system compound, N-methylol system compound, a carbodiimide system compound, and ethylene imino \*\*\*\*\*, are common knowledge. Moreover, when polyvinyl alcohol is chosen as a binder, hardening agents, such as borax, boric acid, borate, resorcinol, a catechol, a phloroglucinol, a gallic acid, vanadium acid, oxalic acid, and N-methylol, are known.

[0059] As a mordant to the water soluble dye used by this invention Polyethyleneimine, JP,57-36692,A, 59-20696, 59-33176, 59-33177, 59-96987, No. 155088 [ 59 to ], 60-11389, 60-49990, 60-83882, 60-109894, 61-277484, 61-293886, 62-19483, 62-198493, 63-49478, 63-115780, 63-203896, 63-274583, 63-280681, 63-260477, The polymer or compound which has the amino group

of the 1-3rd class or the 4th class ammonium indicated by JP,1-9776,A, 1-24784, 1-40371, 3-133686, 6-234268, 7-125411, etc. is used preferably.

[0060] It is desirable that light-fast degradation, small moreover, uses the basic latex polymer which has the 3rd class amino group or the 4th class ammonium among these comparatively as a mordant which has firm color mordancy.

[0061] The basic latex polymer which has the 3rd class or the 4th class nitrogen atom preferably used for this invention is expressed with the following general formula (L).

[0062]

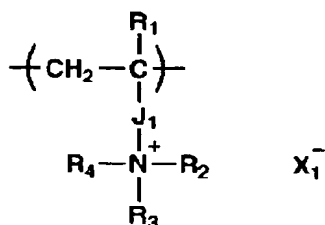
A general formula (L) A expresses the repeating unit guided from the monomer which has the 3rd class amino group or the 4th class ammonium, and which can be copolymerized among a (A)<sub>x</sub>-(B)<sub>y</sub>-(C)<sub>z</sub> type, B expresses the repeating unit guided from the monomer which has at least two ethylene nature partial-saturation radicals, and which can be copolymerized, and C expresses the repeating unit guided from the monomer which has ethylene nature partial-saturation radicals other than A and B at least, which can be copolymerized. x is [ z of y ] 0-90-mol % 0-10-mol% 10-98-mol%.

[0063] a general formula (L) — setting — A — especially — desirable — the following general formula (LA-1), (LA-2), and (LA-3) — or (LA-4) (LA-5) it is expressed.

[0064]

[Formula 1]

—般式(LA-1)

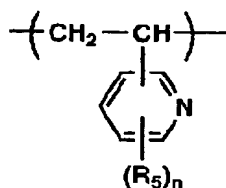


[0065] R1 expresses the alkyl group of a hydrogen atom or the carbon atomic numbers 1-4 among a formula. J1 expresses a divalent connection radical and expresses the benzyl which is not permuted [ a permutation or ] or -COY-. A carbon atomic number is the divalent connection radical of 1-20, for example, Y expresses an alkylene group, an arylene radical, a -O-Y'-radical, and a -NH-Y'-radical (Y' is an alkylene group, an arylene radical, an aralkylene group, etc.). R2, R3, and R4 may express the alkyl group of the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18 respectively, and these alkyl groups or an aralkyl radical may have a substituent. X1- expresses an anion, for example, expresses halogen ion, alkyl sulfonic-acid ion, aryl sulfonic-acid ion, acetic-acid ion, etc.

[0066]

[Formula 2]

—般式(LA-2)

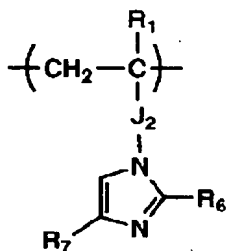


[0067] R5 expresses among a formula the alkyl group which has a hydrogen atom, an alkyl group, an aralkyl radical, or a hydrogen atom, and n expresses the integer of 1-4. when n is two or more, two or more R5 may be the same, or may differ.

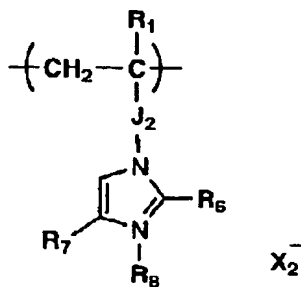
[0068]

[Formula 3]

### 一般式(LA-3)



### 一般式(LA-4)

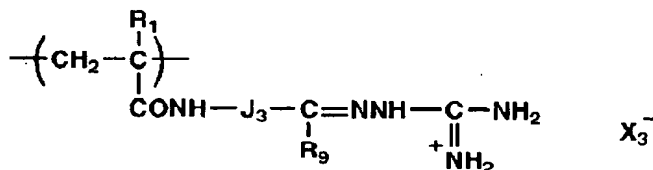


[0069] J2 expresses a mere joint hand or divalent connection radicals (an alkylene group, an arylene radical, aralkylene group, etc.) among a formula. R1 is synonymous with R1 of a general formula (LA-1), and R6 and R7 express a hydrogen atom, an alkyl group, or an aralkyl radical respectively. R8 expresses an alkyl group or an aralkyl radical. X2<sup>-</sup> expresses an anion.

[0070]

[Formula 4]

### 一般式(LA-5)



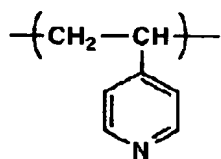
[0071] R1 is synonymous with R1 of a general formula (LA-1) among a formula, and R9 expresses an alkyl group. J3 expresses a mere joint hand or divalent connection radicals (the alkylene group which may have a substituent, respectively, an arylene radical, or aralkylene group). X3- expresses an anion.

[0072] The example of representation of the monomer which forms the repeating unit expressed with general formula (LA-1) – (LA-5) is shown below.

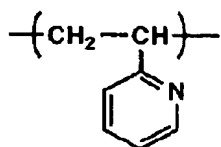
[0073]

[Formula 5]

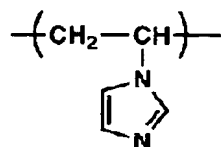
M-1



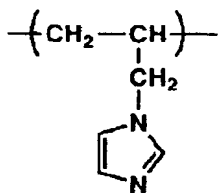
M-2



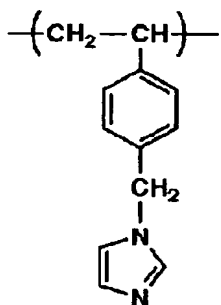
M-3



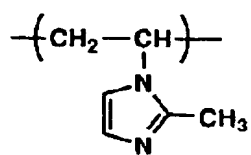
M-4



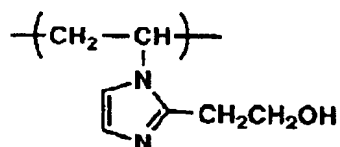
M-5



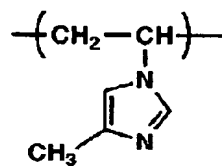
M-6



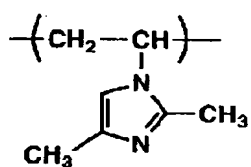
M-7



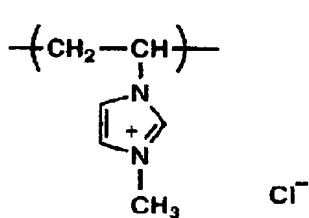
M-8



M-9

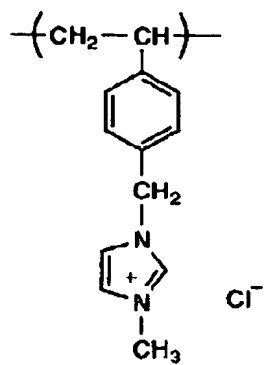


M-10

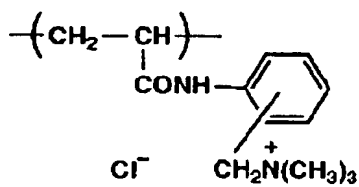


[0074]  
[Formula 6]

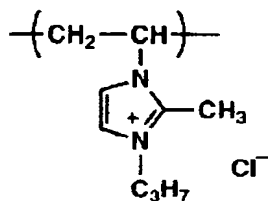
M-11



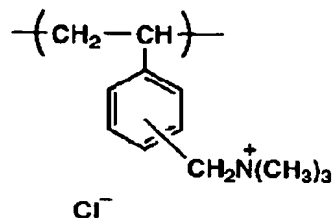
M-15



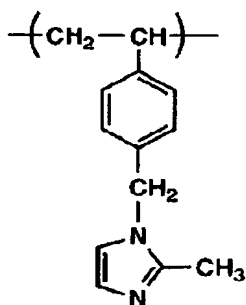
M-12



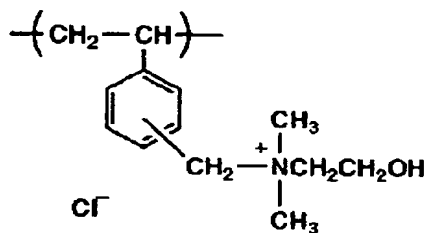
M-16



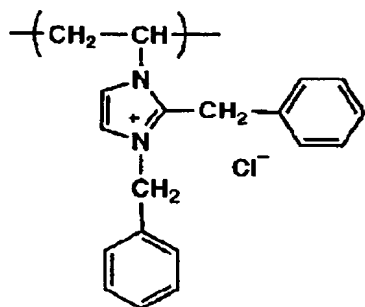
M-13



M-17



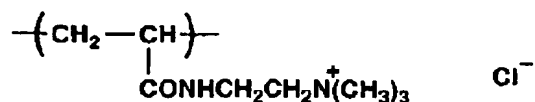
M-14



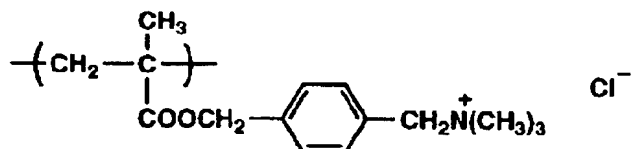
[0075]

[Formula 7]

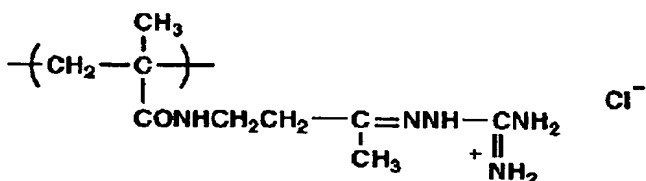
M-18



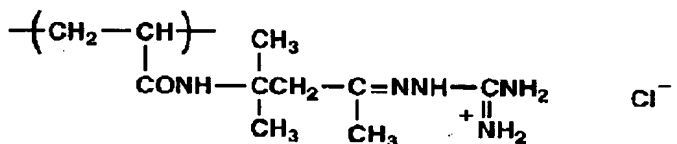
M-19



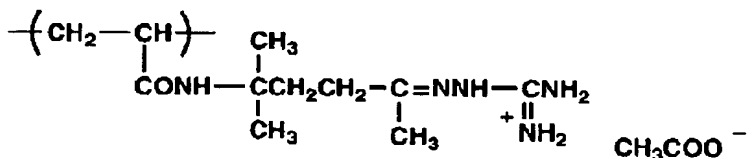
M-20



M-21



M-22



[0076] In a general formula (L), a divinylbenzene, ethylene glycol dimethacrylate, trimethylolpropane triacrylate, tetramethylene glycol diacrylate, propylene glycol dimethacrylate, etc. are mentioned as an example of the monomer which forms the repeating unit expressed with B. Moreover, as an example of the monomer which forms the repeating unit expressed with C, ethylene, 1-butene, styrene, an acrylic acid, a methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl acrylate, t-butyl acrylate, octyl acrylate, benzyl acrylate, acrylic nitril, a maleic acid, vinyl acetate, acrylamide, hydroxymethyl methacrylate, etc. are mentioned.

[0077] The example of a basic latex expressed with a general formula (L) is shown below. However, the monomer showed A, B, and C in a table, respectively.

[0078]

[A table 1]

番号	A	B	C	x	y	z
L-1	M-1	-	C-2	70	0	25
			C-5			5
L-2	M-3	B-1	C-2	70	4	26
L-3	M-5	B-1	C-2	70	4	26
L-4	M-3	B-1	C-4	76	4	20
L-5	M-3	B-1	C-1	70	4	26
L-6	M-5	B-1	C-1	70	4	26
L-7	M-5	B-2	C-1	70	4	26
L-8	M-3	B-1	C-1	40	4	26
	M-12			30		
L-9	M-5	B-1	C-7	70	4	26
L-10	M-5	B-1	C-1	60	2	20
			C-5			18
L-11	M-11	B-1	C-2	70	4	26
L-12	M-15	-	C-2	60	-	40
L-13	M-15	B-1	C-2	60	2	38

[0079]

[A table 2]

番号	A	B	C	x	y	z
L-14	M-15	-	C-6	65	-	35
L-15	M-16	-	C-2	75	-	25
L-16	M-18	B-1	C-1	70	4	26
L-17	M-16	B-1	C-1	70	4	16
			C-4			10
L-18	M-18	B-1	C-1	70	3	15
			C-4			12
L-19	M-18	B-1	C-1	65	4	19
			C-5			12
L-20	M-18	B-1	C-3	60	4	36
L-21	M-21	-	C-6	60	-	40
L-22	M-21	B-1	C-4	60	2	38
L-23	M-22	-	C-8	60	-	40
L-24	M-22	-	C-4	60	-	40
L-25	M-22	-	C-6	60	-	40
L-26	M-22	B-1	C-8	60	-	40

[0080] B-1 to B-2 in a table and C-1 to C-8 show the following.

[0081] B-1: Divinylbenzene B-2 : acrylamide C-7:N-vinyl-pyrrolidone C-8:N- ethylene glycol dimethacrylate C-1: — styrene — C-2:butyl acrylate C-3:t-butyl acrylate — C-4:vinyl acetate C-5:hydroxy MECHICHIRU methacrylate C-6 — (2-acetyl - 1, 1, - dimethyl ethyl) the amount of the mordant used in acrylamide this invention — 1m of record forms — 0.2-5g 0.1-10g per two is the range of 0.5-3g especially preferably preferably.

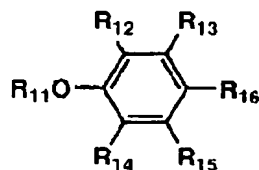
[0082] As for the ink jet record form used for this invention, it is desirable to make an image stabilizer contain in order to raise the lightfastness of water soluble dye. A water-soluble thing may be chosen and you may mix to coating liquid, and an image stabilizer may carry out oil distribution of the oil solubility thing, may make it an oil droplet, and may be mixed to coating liquid.

[0083] As a desirable image stabilizer, a general formula (ST-I) and (ST-II) the compound expressed are mentioned.

[0084]

[Formula 8]

一般式(ST-I)



[0085] R11 expresses a hydrogen atom, an alkyl group, an alkenyl radical, or an aryl group among a formula, and R12, R13, R14, R15, and R16 express a hydrogen atom, a halogen atom, a cyano group, a nitro group, hydroxyl, a sulfonic group, or a univalent organic radical respectively.

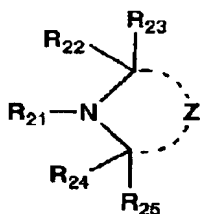
[0086] However, when R11 is a hydrogen atom, R12 and R14 are not hydrogen atoms simultaneously. Moreover, when R11 is an alkyl group, an alkenyl radical, or an aryl group, as for at least one of R12, R13, R14, R15, and the R16, -OR17 (R17 is an alkyl group or an alkenyl radical) or -N (R28)R29, (R28, and R29 are hydrogen atom, alkyl group, or alkenyl radical) respectively.

[0087] Respectively, it may join together mutually and R11, R12 and R12, R13 and R13, R16 and R16, R15 and R15, and R14, R14 and R11 may form a ring.

[0088]

[Formula 9]

一般式(ST-II)



[0089] R21 expresses a hydrogen atom, an alkyl group, an alkenyl radical, a phenyl group, hydroxyl, a sulfonyl group, a sulfinyl group, or an acyl group among a formula, and R22, R23, R24, and R25 express a hydrogen atom or an alkyl group respectively. Z expresses a nonmetal atom group required to form the nitrogen-containing heterocycle of 5 - 7 member.

[0090] Respectively, it may join together mutually and R21, R22 and R22, R23 and R24, and R25, R24 and R21 may form a ring.

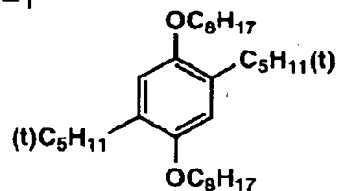
[0091] The example of the especially desirable image stabilizer used for this invention is shown below.

[0092]

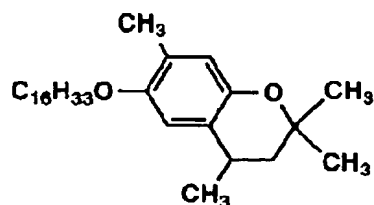
[Formula 10]



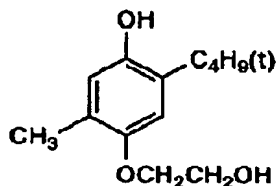
ST-1



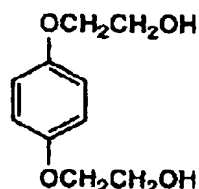
ST-2



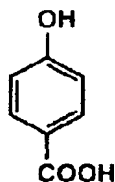
ST-3



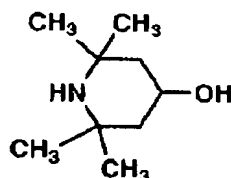
ST-4



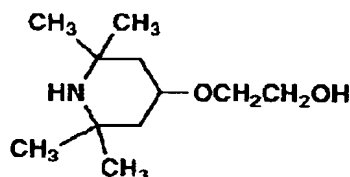
ST-5



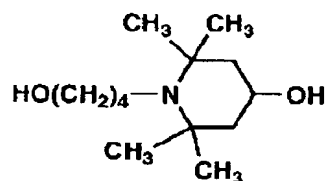
ST-6



ST-7



ST-8



[0093] An ink jet record form can make the compound which absorbs ultraviolet rays in order to raise the lightfastness of water soluble dye contain. As a compound which absorbs ultraviolet rays, the ultraviolet ray absorbent of a publication is mentioned, for example to JP,57-74193,A, 57-87988, 62-261476, etc. In order to make it ultraviolet rays not reach the water soluble dye which exists in a mordant layer, it is effective to see these ultraviolet ray absorbents from a base material rather than a mordant layer, and to make a far layer contain.

[0094] Further various kinds of additives can be made to contain if needed in the layer of the arbitration by the side of the ink receptiveness layer of an ink jet record form. For example, well-known additives, such as lubricant, such as pH regulators, such as the fluorescent brightener indicated by an anion, a cation or the various surfactants of Nonion, JP,59-42993,A, 59-52689, 62-280069, 61-242871, JP,4-219266,A, etc., a sulfuric acid, phosphoric acid, citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, and a diethylene glycol, antiseptics, a thickener, a hardening agent, an antistatic agent, and a mat agent, can also be

made to contain.

[0095] Although especially a limit does not have the amount of the spreading solid content by the side of the ink recording surface in an ink jet record form, 5 – 60 g/m<sup>2</sup> is desirable in general, and 10 – 40 g/m<sup>2</sup> is more desirable. in addition, \*\*\*\* which consists of the field of the curl prevention after record image formation — forming thinly is desirable.

[0096] As a base material of an ink jet record form, the base material which does not absorb water at all substantially among things well-known as a record form for ink jets can be used suitably conventionally.

[0097] The thing of a property which bears the radiant heat when the film which consists of ingredients, such as polyester system resin, diacetate system resin, triacetate system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, being mentioned as a transparence base material, and being used as an OHP also in this is desirable, and especially polyethylene terephthalate (PET) is desirable. As thickness of a transparence base material, about 10–200 micrometers is desirable. It is desirable from an adhesive viewpoint of an ink absorbing layer, a back layer, and a base material to prepare a well-known undercoating layer in an ink absorbing layer [ of a base material ] and back layer side.

[0098] Moreover, the so-called White pet which adds white pigments to the resin coat paper (the so-called RC paper) and PET which have the polyolefin resin enveloping layer which added white pigments etc., and grows at least into one side of a base paper as an opaque base material at them is desirable.

[0099] The approach of applying a hydrophilic layer on a base material can be suitably chosen from a well-known approach, and can be performed. On a base material, a desirable approach paints and dries the coating liquid containing the hydrophilic binder in which sol gel transformation like gelatin is possible, and obtains it. A hydrophilic binder layer has desirable simultaneous spreading which may exist more than two-layer, can also apply more than two-layer simultaneously in this case, and substitutes all hydrophilic binder layers for one spreading especially.

[0100] For example, after cooling and making into the gel state hydrophilic binder content ink absorbing layers in which sol gel transformation is possible, such as gelatin which is indicated by JP,6-64306,A, after applying on a base material, the approach of drying by the cold dry cleaning method is one of the desirable approaches.

[0101] The extrusion coat method which uses the hopper of a publication for the roll coating method, a rod bar coating method, the air-knife-coating method, a spray coating method, the curtain applying method, or a U.S. Pat. No. 2,681,294 number as a spreading method is used preferably.

[0102] the ink jet recording method in which the regurgitation [ water-soluble ink ] of the regurgitation method of the ink used for the ink jet record approach is possible — it is — \*\*\*\*ing — for example, Koichi Nakamura editing — recording methods, such as a continuation injection electrification control system, a method on demand, etc. of a publication, can be used for work "trend of ink jet record technique" (Japanese science-information company \*\*, 1995) 1–14 page. Bigger effectiveness can be acquired by using it also in these, applying to the recording method of a method on demand.

[0103] Water-soluble ink is ink which contains water soluble dye as main sources of coloring, and contains water and a hydrophilic solvent.

[0104] The ink maximum delivery in this invention is the maximum of the amount of ink volume per [ which can be used when the ink jet printer used for this invention outputs all the usual images ] unit area. For example, it is not necessarily the ink maximum delivery which added the amount of ink for obtaining the maximum density of yellow, Magenta, cyanogen, and black each monochrome in the case of the printer for color pictures.

[0105] An ink maximum delivery can be calculated by count, if the volume of one drop of liquid ink drop is known and the array approach of the drop for forming an image is known.

**\* NOTICES \***

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**EXAMPLE**

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[Example] Although the example of this invention is given and explained below, this invention is not limited to these. In addition, "%" in an example shows oven-dry-weight %, as long as there is no notice especially, and an addition shows the amount per two 1m of ink jet record forms.

[0107] the paper base material (the inside of the polyethylene layer by the side of 140 micrometers in thickness, and a recording surface — 7% of the weight of anatase mold titanium-dioxide content — carrying out — the rear-face side of a recording surface — as a back layer) which covered 100g/stencil both sides of m2 with polyethylene It multilayer-simultaneous-applied and the coating liquid of the presentation shown in tables 3, 4, 5, and 6 at a recording surface side, respectively in [ having a layer containing alkali treatment gelatin 1.2 g/m2 and a hardening agent ] was dried, it adjusted so that it might become the desiccation thickness and void volume in a table, and the record forms 1-11 were obtained.

[0108] In addition, the void volume in a record form was calculated as follows. That is, the cross section of a sample is observed with an optical microscope, an electron microscope, etc., and the thickness of an ink absorbing layer is measured. Since the volume of solid content can be known from the presentation of this ink absorbing layer, the thickness when presupposing that the opening is not made is calculable. Since the difference of this measured value and calculated value is the thickness which increased by the opening, that void volume can be known by count.

[0109]

[A table 3]

記録用紙 1			
上層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 界面活性剤-1 界面活性剤-2	790ml 40 g 25 g 0.7 g 0.3 g	乾燥膜厚 0.5 $\mu$ m
中層	純水 炭酸カルシウム（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	500ml 192 g 12.8 g 1.2 g	空隙容量 20ml/m <sup>2</sup>
下層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤-1 界面活性剤-1 界面活性剤-2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu$ m
記録用紙 2			
上層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 界面活性剤-1 界面活性剤-2	790ml 40 g 25 g 0.7 g 0.3 g	乾燥膜厚 0.5 $\mu$ m
中層	純水 微粒子シリカ（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2 g 12.8 g 1.2 g	空隙容量 20ml/m <sup>2</sup>
下層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤-1 界面活性剤-1 界面活性剤-2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu$ m

PCゼラチン：フェニルカルバモイル化ゼラチン

PVA：ポリビニルアルコール

[0110]

[A table 4]

記録用紙 3			
上層	純水	790ml	乾燥膜厚 2.0 $\mu\text{m}$
	PCゼラチン (アミノ基封鎖率: 約88%)	40 g	
	PVA	25 g	
	媒染剤-1	10 g	
	界面活性剤-1	0.7 g	
	界面活性剤-2	0.3 g	
下層	純水	980ml	空隙容量 20ml/ $\text{m}^2$
	微粒子シリカ (平均粒径: 約0.07 $\mu\text{m}$ )	48.2 g	
	PVA (鹸化度: 89%, 平均重合度: 2,350)	12.8 g	
	界面活性剤-3	1.2 g	
記録用紙 4			
上層	純水	980ml	空隙容量 20ml/ $\text{m}^2$
	微粒子シリカ (平均粒径: 約0.07 $\mu\text{m}$ )	48.2 g	
	PVA (鹸化度: 89%, 平均重合度: 2,350)	12.8 g	
	界面活性剤-3	1.2 g	
下層	純水	790ml	乾燥膜厚 2.0 $\mu\text{m}$
	PCゼラチン (アミノ基封鎖率: 約88%)	40 g	
	PVA	25 g	
	媒染剤-1	10 g	
	界面活性剤-1	0.7 g	
	界面活性剤-2	0.3 g	
記録用紙 5			
上層	純水	980ml	空隙容量 20ml/ $\text{m}^2$
	微粒子シリカ (平均粒径: 約0.07 $\mu\text{m}$ )	48.2 g	
	PVA (鹸化度: 89%, 平均重合度: 2,350)	12.8 g	
	界面活性剤-3	1.2 g	
下層	純水	790ml	乾燥膜厚 2.0 $\mu\text{m}$
	PCゼラチン (アミノ基封鎖率: 約88%)	40 g	
	PVA	25 g	
	媒染剤-1	10 g	
	界面活性剤-1	0.7 g	
	界面活性剤-2	0.3 g	

[0111]

[A table 5]

記録用紙 6			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu\text{m}$ ） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤－3	930ml 140 g 12.8 g 1.2 g	空隙容量 20ml/ $\text{m}^2$
下層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤－1 界面活性剤－1 界面活性剤－2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu\text{m}$
記録用紙 7			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu\text{m}$ ） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤－3	980ml 48.2 g 12.8 g 1.2 g	空隙容量 20ml/ $\text{m}^2$
下層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤－2 界面活性剤－1 界面活性剤－2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu\text{m}$
記録用紙 8			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu\text{m}$ ） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤－3	980ml 48.2 g 12.8 g 1.2 g	空隙容量 20ml/ $\text{m}^2$
下層	純水 酸処理ゼラチン PVA 媒染剤－1 界面活性剤－1 界面活性剤－2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu\text{m}$

[0112]

[A table 6]

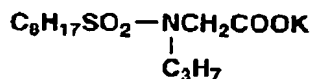
記録用紙 9			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2g 12.8g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 酸処理ゼラチン PVA 媒染剤-1 硬膜剤-1 界面活性剤-1 界面活性剤-2	790ml 40g 25g 10g 2g 0.7g 0.3g	乾燥膜厚 2.0 $\mu$ m
記録用紙10			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2g 12.8g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 酸処理ゼラチン PVA 媒染剤-1 画像安定剤（例示ST-5） 硬膜剤-1 界面活性剤-1 界面活性剤-2	780ml 40g 25g 10g 10g 2g 0.7g 0.3g	乾燥膜厚 2.0 $\mu$ m
記録用紙11			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 分散物-1 界面活性剤-3	980ml 48.2g 12.8g 5g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 酸処理ゼラチン PVA 媒染剤-1 硬膜剤-1 界面活性剤-1 界面活性剤-2	780ml 40g 25g 10g 2g 0.7g 0.3g	乾燥膜厚 2.0 $\mu$ m

[0113] The structure of the raw material used for record form production is as follows.

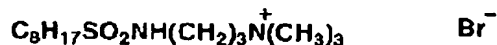
[0114]

[Formula 11]

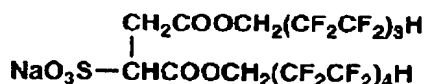
界面活性剂-1



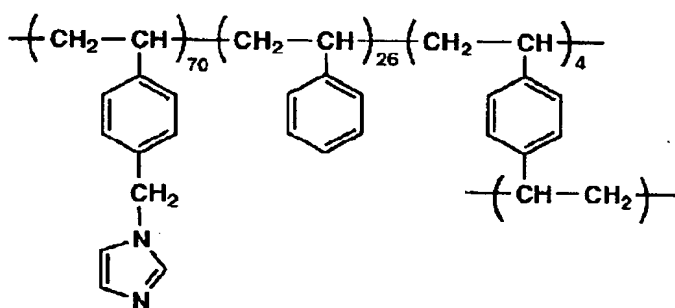
界面活性剂-2



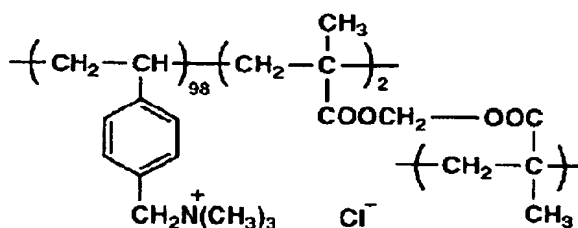
界面活性剂-3



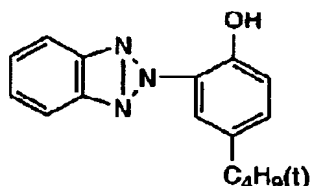
媒染剂-1



媒染剂-2



紫外線吸収剂-1



[0115] (Distributed object -1) The solution 1 and solution 2 of the following presentation were prepared, and it mixed, and distributed in the ultrasonic disperser.

[0116] Solution 1 ultraviolet ray absorbent -1 1g G i-DESHIRU phthalate 1g ethyl acetate 5ml solution 2PC gelatin (thing given in a table) 0.5g surfactant -4 0.2g pure water 15ml surfactant -4: To the record forms 1-11 of the tree i-propyl naphthalene sulfonic-acid sodium above, it is a line with a monochrome solid [ of a Magenta ], and a width of face of 1mm with an ink jet printer on demand. It printed. Printing environments are the room temperature of 23 degrees C, and 50% of relative humidity, and ink discharge quantity is 21 ml/m2.

[0117] The following items estimated to the obtained pattern and the result shown in a table 7 was obtained.

[0118] The sample of the maximum-density part of a << lightfastness >> Magenta was asked for



the ratio of the reflection density before 24-hour Mitsuteru putting, and an exposure after an exposure in xenon fade meter.

[0119] The << water resisting property >> printing sample was dried after being immersed for 10 minutes into 20-degree C water, and residual concentration compared the water resisting property of the printing image of the maximum-density part of a Magenta color. O evaluated what has high concentration and the low thing was evaluated in four steps of x.

[0120] After saving the sample after << moisture resistance >> printing for two weeks at 23 degree C and 20% of relative humidity, it saved for three days at 60 degree C and 80% of relative humidity, and the blot degree of each color was investigated.

[0121] Assessment carried out the visual judgment of the flare of a line before and after saving at 60 degree C and 80% of relative humidity on the following criteria.

[0122]

O : blot-less O:blot width of face is completely less than (extent a blot is slightly accepted to be in feeling of \*\*) about 0.1mm.

\*\* : Blot width of face is 0.1mm - less than (allowance is impossible in feeling of \*\*) 0.5mm.

x : Blot width of face is 0.5mm or more (level which does not almost have the value as an image).

The visual judgment of the degree of the ink which the load of superposition and 100 g/cm<sup>2</sup> was applied, left the rear face of the same record form for 1 minute, and imprinted it at the rear face to the printing side after [ of an after / << drying >> printing ] 2 minutes was carried out on the following criteria.

[0123]

O : — completely — imprint-less O: — although there is an imprint faintly — a subject-copy image — almost — effect-less x: — a lot of ink imprinted, and the subject-copy image carried out 20-point density measurement of the solid section of a << concentration nonuniformity >> printing sample which does not bear admiration by the microdensitometer (the diameter of an aperture: 200 micrometers), and asked for the standard deviation of a concentration value.

[0124]

[A table 7]

記録用紙No.	耐光性	耐水性	耐湿性	乾燥性	濃度ムラ
1 (本発明)	60	△	○	○	0.4
2 (本発明)	75	△	○	○	0.6
3 (比較例)	30	○	○	○	0.9
4 (比較例)	25	×	×	×	1.5
5 (本発明)	75	△	△	○	0.1
6 (本発明)	80	△	△	◎	0.0
7 (本発明)	75	△	○	○	0.1
8 (本発明)	70	○	○	○	0.1
9 (本発明)	70	◎	○	○	0.1
10 (本発明)	90	◎	○	○	0.1
11 (本発明)	95	◎	○	○	0.1

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(54)【発明の名称】 インクジェット記録用紙

(57)【要約】

【課題】 水溶性染料を用いたインクジェット記録用紙の改善、即ち、迅速なインクの吸収による高画質記録が可能で、記録後の染料の耐水性や耐湿性を改良し、しかも耐光性を低下させないインクジェット記録用紙を提供する。

【解決手段】 水を実質的に全く吸収しない支持体上に、水溶性染料を固定する媒染剤含有層と該媒染剤含有層より支持体から離れた側に設けられた空隙層を有し、該空隙層の空隙容量がインク最大吐出量の 90%以上有することを特徴とするインクジェット記録用紙。

**【特許請求の範囲】**

【請求項1】 水を実質的に全く吸収しない支持体上に、水溶性染料を固定する媒染剤含有層と該媒染剤含有層より支持体から離れた側に設けられた空隙層を有し、該空隙層の空隙容量がインク最大吐出量の90%以上有することを特徴とするインクジェット記録用紙。

【請求項2】 支持体から最も遠い層が空隙層であることを特徴とする請求項1記載のインクジェット記録用紙。

【請求項3】 媒染剤含有層のバインダーが硬膜されていることを特徴とする請求項1又は2記載のインクジェット記録用紙。

【請求項4】 媒染剤が3級アミン系ポリマー又は4級アンモニウム塩系ポリマーであることを特徴とする請求項1、2又は3記載のインクジェット記録用紙。

【請求項5】 媒染剤含有層に酸処理ゼラチンを含有することを特徴とする請求項4記載のインクジェット記録用紙。

【請求項6】 媒染剤含有層に画像安定剤を含有することを特徴とする請求項4又は5記載のインクジェット記録用紙。

【請求項7】 支持体に対し媒染剤含有層よりも遠い側にある層に、紫外線を吸収する化合物を含有することを特徴とする請求項4、5又は6記載のインクジェット記録用紙。

【請求項8】 空隙層中の無機微粒子とバインダーの体積比が5以上であることを特徴とする請求項1～7のいずれか1項に記載のインクジェット記録用紙。

【請求項9】 空隙層が、無機固体微粒子を塗布液調製時又は皮膜形成時に凝集させ、3次元構造を形成させて得られたものであることを特徴とする請求項1～8のいずれか1項に記載のインクジェット記録用紙。

**【発明の詳細な説明】****【0001】**

【発明の属する技術分野】本発明は水溶性染料を用いて記録を行うインクジェット記録用紙に関し、特にインク吸収性を改善したインクジェット記録用紙に関するものである。

**【0002】**

【従来の技術】インクジェット記録は、インクの微小液滴を種々の作動原理により飛翔させて紙などの記録シートに付着させ、画像・文字などの記録を行うものであるが、比較的に高速、低騒音、多色化が容易である等の利点を有している。この方式で従来から問題となっていたノズルの目詰まりとメンテナンスについては、インク及び装置の両面から改良が進み、現在では各種プリンター、ファクシミリ、コンピューター端末等、様々な分野で急速に普及している。

【0003】このインクジェット記録方式で使用する記録用紙としては、印字ドットの濃度が高く、色調が明

るく鮮やかであること、インクの吸収が早く印字ドットが重なった場合においてもインクが流れ出したり滲んだりしないこと、印字ドットの横方向への拡散が必要以上に大きくなく、かつ周辺が滑らかでぼやけないこと等が要求される。

【0004】特にインク吸収速度が遅い場合には、2色以上のインク液滴が重なって記録される際に、記録用紙上で液滴がハジキ現象を起こしてムラになったり、又、異なる色の境界領域で互いの色が滲んだりして画質を大きく低下させ易いために、記録用紙としては高いインク吸収性を持つことが必要である。

【0005】これらの問題を解決するために、従来から非常に多くの技術が提案されている。例えば、特開昭52-53012号に記載される低サイズ原紙に表面加工用の塗料を湿潤させた記録用紙、特開昭55-5830号に記載される支持体表面にインク吸収性の塗層を設けた記録用紙、特開昭56-157号に記載される被覆層中の顔料として非膠質シリカ粉末を含有する記録用紙、特開昭57-107878号に記載される無機顔料と有機顔料を併用した記録用紙、特開昭58-110287号に記載される二つの空孔分布ピークを有する記録用紙、特開昭62-111782号に記載される上下2層の多孔質層から成る記録用紙、特開昭59-68292号、同59-123696号及び同60-18383号等に記載される不定形亀裂を有する記録用紙、特開昭61-135786号、同61-148092号及び同62-149475号等に記載される微粉末層を有する記録用紙、特開昭63-252779号、特開平1-108083号、同2-136279号、同3-65376号及び同3-27976号等に記載される特定の物性値を有する顔料や微粒子シリカを含有する記録用紙、特開昭57-14091号、同60-219083号、同60-210984号、同61-20797号、同61-188183号、特開平5-278324号、同6-92011号、同6-183134号、同7-137431号、同7-276789号等に記載されるコロイド状シリカ等の微粒子シリカを含有する記録用紙、特開平2-276671号、同3-67684号、同3-215082号、同3-251488号、同4-67986号、同4-263983号及び同5-16517号等に記載されるアルミナ水和物微粒子を含有する記録用紙など多数が知られている。

【0006】しかし、インク受容層がインクを吸収したり保持するための空隙を多く有する層のみから構成される場合、空隙の多いインク受容層が空気との界面や皮膜表面のミクロな凹凸を多く有することになり、インク受容層への入射光が散乱されたり、透過が妨げられるために、光沢が出難くなったり不透明になり易い。

【0007】又、空隙を形成するため顔料自身の凹凸や顔料の2次凝集体の凹凸による皮膜表面の平滑性が低下

して光沢が出難い欠点がある。

【0008】一方、皮膜中に空隙を設けることなく、インク吸収層のバインダーの膨潤作用でインクを吸収、保持するタイプのインクジェット記録用紙も数多く知られている。例えば、バインダーとしてゼラチン、カゼイン、澱粉、アルギン酸、ポリビニルアルコール、各種の変成ポリビニルアルコール、ポリビニルピロリドン、ポリエチレンオキサイド、ポリプロピレンオキサイド、カルボキシメチルセルロース、ヒドロキエチルセルロース、デキストラン、プルラン等の親水性バインダーを支持体上に塗布した記録紙やフィルム等も従来から数多く知られている。

【0009】これらの記録用紙は、インク吸収性が上記空隙を有する記録用紙に比べて劣るものの、高い光沢性や光学濃度、鮮明な画像が得られ、高画質記録用途として有用である。

【0010】以上の二つのタイプを組み合わせたとしたとして、特開平7-186521号に、水溶性樹脂から成る下層に親水性樹脂と無機微粒子及び充填剤から成る上層を積層したインクジェット記録用紙が記載されている。又、特開昭61-12388号、同61-35275号、同61-49883号、同61-49884号、同61-49885号、同61-135787号、同61-135788号、同62-196175号、同62-222887号等にあるように、インク透過層をインク保持層よりも上層に設けたインクジェット記録用紙が知られている。

【0011】上記の水溶性インクに適した各種のインクジェット記録用紙においては、色素分子が油剤中に高濃度の微粒子状態で分散されているカラー印画紙等と異なり、色素分子が単独でバインダー中や空隙間に存在するために、水滴が記録面にかかったり、印字後に高湿度条件下で長期間保存された際に色素が滲んだり流れ出したりし易い欠点があった。

【0012】この色素の耐水性や耐湿性を改良するために、従来から色素をバインダー中に固定させる種々の方法が提案されている。特に有効な手段は、3級又は4級の窒素原子を有するポリマーを均一な水溶液として、又は微粒子ラテックスとして添加する方法である。

【0013】例えば特開昭57-36692号には、ゼラチンをバインダーの一部として塩基性媒染剤を含有する塗布液をインク受容層として原紙やポリエチレンテレフタレート（PET）フィルム支持体上に塗布したインクジェット記録用紙が記載されている。

【0014】又、特開昭53-49113号には、紙内にポリエチレンイミンを含浸させた水性インキ記録用紙；特開昭58-24492号には、カチオン又はアニオン基を有する電解質ポリマーを有する記録材料；特開昭63-224988号には、インク受容層内に第1級～第3級アミン又は第4級アンモニウム塩を含有し、イ

ンク保持層のpHが2～8にある被記録材料；特開昭63-307979号には、3級又は4級窒素原子を有する親水性ポリマー媒染剤と親水性基を有する重合体を含有する層を有するインクジェット記録シート；特開昭59-198186号及び同59-198188号には、ポリエチレンイミンの有機塩基を基材中又は基材上の塗工層中に含有させた被記録材料；特開昭60-46288号には、特定染料を含有するインクとポリアミン等を含有する記録材料を用いたインクジェット記録方法；特開昭61-61887号、同61-72581号、同61-252189号及び同62-174184号には、ポリアリルアミンを含有するインクジェット記録用紙；特開昭61-172786号には、分子間水素結合を有するポリマー（ゼラチン、ポリエチレンイミン等）と分子間に水素結合性基を有しないポリマー（ポリエチレングリコール、ポリビニルピロリドン等）を含有するインクジェット記録材料；特開昭63-162275号には、カチオン性ポリマーとカチオン性界面活性剤を支持体上に塗布又は含浸させたインクジェット記録用紙；特開平6-143798号には、プラスチック支持体上に第4級アンモニウム塩重合体とカチオン変成ポリビニルアルコールを主成分とする染料定着層と、その上に設けられた染料透過・インク吸収層を重畳した記録シートが記載されている。

【0015】これらの染料固着能を持つポリマーを空隙層に組み込むことは、調液・塗布中に増粘や凝集を起こすことが多く一般に困難である。又、仮に組み込んだとしても空隙層に染料が固着されるため、染料が空気中の酸素に晒されて耐光性を劣化させる傾向がある。これらの理由から、従来、染料固着能を持つポリマーを空隙層に組み込むことは少なかった。

【0016】一方、皮膜中に空隙を設けることなくインク吸収層のバインダーの膨潤作用でインクを吸収、保持するタイプのインクジェット記録用紙に関しては、比較的容易に上記の染料固着能を持つポリマーを組み込むことが可能である。しかし、前述の通り、このタイプの水溶性バインダーから成る層はインクの吸収性が遅いことが問題である。

【0017】

【発明が解決しようとする課題】本発明は上記の実態に鑑みてなされたものであって、本発明の目的は、水溶性染料を用いたインクジェット記録用紙の改善にあり、迅速なインクの吸収による高画質な記録が可能で、記録後の染料の耐水性や耐湿性を改良し、しかも耐光性を低下させないインクジェット記録用紙を提供することにある。

【0018】

【課題を解決するための手段】上記本発明の目的は、以下の構成によって達成される。

【0019】（1）水を実質的に全く吸収しない支持体

上に、水溶性染料を固定する媒染剤含有層と該媒染剤含有層より支持体から離れた側に設けられた空隙層を有し、該空隙層の空隙容量がインク最大吐出量の90%以上有するインクジェット記録用紙。

【0020】(2) 支持体から最も遠い層が空隙層である(1)に記載のインクジェット記録用紙。

【0021】(3) 媒染剤含有層のバインダーが硬膜されている(1)又は(2)に記載のインクジェット記録用紙。

【0022】(4) 媒染剤が3級アミン系ポリマー又は4級アンモニウム塩系ポリマーである(1)、(2)又は(3)に記載のインクジェット記録用紙。

【0023】(5) 媒染剤含有層に酸処理ゼラチンを含む(4)に記載のインクジェット記録用紙。

【0024】(6) 媒染剤含有層に画像安定剤を含む(4)又は(5)に記載のインクジェット記録用紙。

【0025】(7) 支持体に対し媒染剤含有層よりも遠い側にある層に、紫外線を吸収する化合物を含む(4)、(5)又は(6)に記載のインクジェット記録用紙。

【0026】(8) 空隙層中の無機微粒子とバインダーの体積比が5以上である(1)～(7)のいずれか1項に記載のインクジェット記録用紙。

【0027】(9) 空隙層が、無機固体微粒子を塗布液調製時又は皮膜形成時に凝集させ、3次元構造を形成させて得られたもので(1)～(8)のいずれか1項に記載のインクジェット記録用紙。

【0028】以下、本発明をより詳細に説明する。

【0029】本発明に用いるインクジェット記録用紙が有する空隙層は、親水性又は疎水性のバインダー、無機又は有機の固体粒子、あるいは油滴等の固体成分とその間に形成される空隙から成る。

【0030】空隙の形成は種々の方式で行うことができ、その方法により空隙層が含有する固体成分も異なるのが一般的である。以下に代表的な空隙層の形成方法について説明する。

【0031】①2種以上のポリマーを含む均一な塗布液を支持体上に塗布し、乾燥過程で、これらのポリマーを互いに相分離させて空隙を形成する方法

②固体微粒子及び親水性又は疎水性バインダーを含む塗布液を支持体上に塗布・乾燥後に記録用紙を水あるいは適当な有機溶媒を含む液に浸漬して固体微粒子を溶解させて空隙を作成する方法

③皮膜形成時に発泡する性質を有する化合物を含む塗布液を塗布後、乾燥過程で、この化合物を発泡させて皮膜中に空隙を形成する方法

④多孔質固体微粒子及び親水性バインダーを含む塗布液を支持体上に塗布し、多孔質微粒子中や微粒子間に空隙を形成する方法

⑤親水性バインダーに対して概ね等量以上(好ましくは

1.0倍以上)の容積を有する固体微粒子及び/又は微粒子油滴と親水性バインダーを含む塗布液を支持体上に塗布して固体微粒子の間に空隙を作成する方法

⑥平均粒径が約0.1 $\mu\text{m}$ 程度以下の固体微粒子を塗布液調製時又は皮膜形成時に凝集させ、2次粒子又は3次元構造を形成して空隙を作成する方法。

【0032】本発明における空隙形成方法は上記の如何なる手段によってもよいが、記録紙表面の光沢度を余り低下させない方法を用いることが好ましい。そのための空隙の大きさは約0.5 $\mu\text{m}$ 、好ましくは約0.3 $\mu\text{m}$ 、特に好ましくは約0.2 $\mu\text{m}$ 程度以下であり、充填物の大きさや皮膜形成時の製造条件も、このような空隙を形成する条件になるように設定するのが好ましい。

【0033】一方、インクジェット記録用紙を低コストで作成すると言う観点から、複雑な製造工程を取らずに作成できる方法が好ましい。

【0034】以上の観点から、本発明を実施するに当たっての好ましい方法は上記①、⑤及び⑥であり、特に好ましいのは⑤又は⑥の方法である。

【0035】本発明に用いるインクジェット記録用紙の空隙層の空隙容量の総量は、インクの最大吐出量の90%以上であることが必要である。本発明とは異なり、媒染剤を含む層が空隙層より上層にある場合は、空隙層の空隙容量がインクの最大吐出量の90%に満たない場合でも高いインク量の印字の際にインクが溢れ出して乾燥性を悪くする問題は生じない。ところが、空隙層が媒染剤を含む層よりも上層にある場合に限って、高いインク量の印字の際にインクが溢れて画質を低下させたり、あるいは印字後の乾燥性が遅いなどの問題が生じる。

【0036】ここで空隙容量とは、空隙層中の乾燥膜厚から空隙層中のバインダーや各種の充填剤等の固形分の容量の総量を差し引いた値であり、空隙率はこれら固形分の容量に対する空隙量の割合を示す。

【0037】好ましくは空隙率を250容量%以上にするのがよい。空隙率の上限は、充填剤の種類やバインダーの種類により一般に変化するが、皮膜としての強度や脆弱性等から一般には400容量%以下である。

【0038】空隙層が固体微粒子を含む空隙層で有る場合、固体微粒子としては、従来インクジェット記録用紙で公知の各種の無機又は有機の固体微粒子を用いることができる。

【0039】上記無機微粒子の例としては、軽質炭酸カルシウム、重質炭酸カルシウム、炭酸マグネシウム、カオリン、クレー、タルク、硫酸カルシウム、硫酸バリウム、二酸化チタン、酸化亜鉛、水酸化亜鉛、硫化亜鉛、炭酸亜鉛、ハイドロタルサイト、珪酸アルミニウム、珪藻土、珪酸カルシウム、珪酸マグネシウム、合成非晶質シリカ、コロイダルシリカ、アルミナ、コロイダルアルミナ、擬ペーマイト、水酸化アルミニウム、リトポン、

ゼオライト、水酸化マグネシウム等の白色無機顔料等を挙げることができる。その様な無機微粒子は、1次粒子のままでバインダー中に均一に分散された状態で用いられてもよく、又、2次凝集粒子を形成してバインダー中に分散された状態で添加されてもよい。

【0040】一方、有機微粒子の例としては、ポリスチレン、ポリアクリル酸エステル類、ポリメタクリル酸エステル類、ポリアクリルアミド類、ポリエチレン、ポリプロピレン、ポリ塩化ビニル、ポリ塩化ビニリデン、又はこれらの共重合体、尿素樹脂、メラミン樹脂等が挙げられる。

【0041】本発明においては、高い濃度を達成し、鮮明な画像を記録し、低コストで製造できる等の点より、固体微粒子としてアルミナ水和物微粒子、シリカ微粒子及び炭酸カルシウムから選ばれる固体微粒子を用いることが好ましい。

【0042】好ましく用いられるアルミナ又はアルミナ水和物は、半径が3~10nmである細孔容積の和が0.2~2cc/gである多孔質アルミナ又はその含水物である。細孔容積の測定手段は、アルミナ又はアルミナ水和物の乾燥固形分に対して公知の窒素吸着法により測定することができる。

【0043】アルミナ又はアルミナ水和物は、結晶性であっても非晶質であってもよく、又、形状は不定形粒子、球状粒子、針状粒子など任意の形状のものを使用できる。

【0044】本発明に使用されるシリカ系微粒子としては、従来インクジェットで公知の各種のシリカ系微粒子を使用することができ、例えば、湿式又は気相法で合成された合成シリカ、コロイダルシリカ、1次粒子が凝集して2次粒子を形成している多孔質シリカ等、任意の形状のシリカを使用することができる。その様な例として、例えば特開昭55-51583号及び同56-148583号等に記載された合成非晶質シリカ、特開昭60-204390号に記載された気相法により合成されたシリカ超微粒子、特開昭60-222282号に記載された弗素を含有する合成不定形シリカ、特開昭60-224580号及び同62-178384号に記載されたシランカップリング剤により表面処理された合成不定形シリカ、特開昭62-183382号及び同63-104878号に記載された球状シリカ、特開昭63-317381号に記載されたNa<sub>2</sub>O含有量が0.5重量%以上である合成シリカ微粒子、特開平1-115677号に記載された比表面積が100m<sup>2</sup>/g以上の合成シリカ微粒子、特開昭62-286787号に記載されたアルミナ表面処理された合成シリカ微粒子、特開平1-259982号に記載されたCa、Mg又はBaで表面処理された合成シリカ微粒子、吸油量が180cc/g以上k合成シリカ微粒子、特開昭57-14091号に記載されたコロイダルシリカ、特開昭60-2190

84号、特開平6-92011号、同6-297830号及び同7-81214号に記載されたカチオン性コロイダルシリカ、特開平5-278324号及び同7-81214号に記載された数珠状に連結/又は分岐したコロイダルシリカ等を挙げることができる。

【0045】しかしながら、高い光沢性と高い空隙容量を得るためには、平均粒径が7~30nmのシリカ超微粒子を用いることが好ましい。このシリカ微粒子は、表面がカチオン変成されたものでもよく、又、Al、Ca、Mg、Ba等で処理されたものでもよい。

【0046】本発明の記録用紙に用いられる炭酸カルシウムとしては、例えば特開昭5712-486号、同57-129778号、同58-55283号、同61-20792号に記載された特定に比表面積を有する軽質炭酸カルシウム、特開昭63-57277号及び特開平4-250091号に記載された針柱状炭酸カルシウム、特開平3-251487号に記載された特定の針状1次粒子が凝集して2次粒子を形成した炭酸カルシウム微粒子、特開平4-250091号及び同4-260092号に記載された特定の吸油量を有する針柱状の斜方晶アルゴナイト炭酸カルシウム、及び特開平7-40648号に記載された球状沈降性炭酸カルシウム等が挙げられる。高い光沢性と高い空隙容量を得られることから、粒径が約0.1μm以下の炭酸カルシウム微粒子を使用することが好ましく、特に平均粒径が10~50nmの炭酸カルシウム微粒子の使用が好ましい。

【0047】上記空隙層は、皮膜としての特性を維持するためにバインダーを有していることが好ましい。このバインダーとしては従来公知の各種バインダーを使用することができるが、インクのより高い浸透性が得られる親水性バインダーが好ましく用いられる。しかしながら、親水性バインダーの使用に当たっては、インクの初期の浸透時にバインダーが膨潤して空隙を実質的に塞いでしまわないことが重要であり、この観点から比較的室温付近で膨潤性の低い親水性バインダーが好ましい。特に好ましい親水性バインダーは、完全又は部分鹸化のポリビニルアルコール又はカチオン変成ポリビニルアルコールである。

【0048】ポリビニルアルコールの中でも特に好ましいのは、鹸化度が80以上の部分又は完全鹸化したものである。又、皮膜脆弱性を改良する観点から、平均重合度は500~3000、特に好ましくは1000~3000のものが用いられる。

【0049】又、カチオン変成ポリビニルアルコールとしては、例えば特開昭61-10483号に記載されるような、第1~3級アミノ基や第4級アンモニウム基を上記ポリビニルアルコールの主鎖又は側鎖中に有するポリビニルアルコールである。

【0050】又、前記空隙層中には他の親水性バインダーを含有させることができるが、好ましくは、これら親

水性バインダーは、上記ポリビニルアルコール又はカチオン変成ポリビニルアルコールに対して概ね20重量%以下であることが好ましい。

【0051】本発明において特に好ましい態様である、前記⑤又は⑥による空隙作成の場合、固体微粒子の親水性バインダーに対する体積比は3以上、特に5以上にするのが好ましい。ただし、本発明で言う体積とは、重量を真比重で割って求めた体積値であり、粒子内部の空隙を含んだ見かけの体積とは無関係である。

【0052】又、この場合、皮膜の脆弱性を改良するために各種の油滴を含有することが好ましいが、その様な油滴としては、室温における水に対する溶解性が約0.01重量%以下の疎水性高沸点有機溶媒（流動パラフィン、ジオクチルフタレート、トリクレジルホスフェート、シリコンオイル等）や重合体粒子（スチレン、ブチルアクリレート、ジビニルベンゼン、ブチルメタクリレート、ヒドロキシエチルメタアクリレート等の重合性モノマーを1種以上重合させた粒子）を含有させることができる。その様な油滴は、好ましくは親水性バインダーに対して10～50重量%用いることができる。

【0053】空隙層は2層以上から構成されていてもよく、この場合、それらの空隙層の構成は前述した範囲内であれば異なってもよい。

本発明に用いるインクジェット記録用紙は、支持体から最も遠い最上層が空隙層であることが好ましい。これは、インクの吸収が速い空隙層の利点を最大限に生かせるからである。

【0054】インクジェット記録用紙の媒染剤含有層に好ましく用いられるバインダーとしては、ゼラチン又はゼラチン誘導体、ポリビニルピロリドン（平均分子量が約20万以上が好ましい）、プルラン、ポリビニルアルコール又はその誘導体（平均分子量が約2万以上が好ましい）、ポリエチレングリコール（平均分子量が10万以上が好ましい）、カルボキシメチルセルロース、ヒドロキシエチルセルロース、デキストラン、デキストリン、ポリアクリル酸及びその塩、寒天、 $\kappa$ -カラギーナン、 $\lambda$ -カラギーナン、 $\iota$ -カラギーナン、キサンテンガム、ローカストビーンガム、アルギン酸、アラビアガム、プルラン、特開平7-195826号及び同7-9757号に記載のポリアルキレンオキサイド系共重合性ポリマー、水溶性ポリビニルブチラールあるいは特開昭62-245260号に記載のカルボキシル基やスルホ基を有するビニルモノマーの単独又はこれらのビニルモノマーを繰返して有する共重合体等のポリマーを挙げることができる。これらの親水性バインダーは単独で使用してもよく、2種以上を併用してもよい。

【0055】安定高速塗布の観点から、少なくとも1種は可逆的にゾルゲル変換可能な親水性バインダーを一部使用するのが好ましく、例えばゼラチン、ゼラチン誘導体、及び $\kappa$ -カラギーナンの少なくとも1種を使用する

のが好ましい。

【0056】又、耐湿・耐水性に、より効果的なバインダーとして酸処理ゼラチンが挙げられる。酸処理ゼラチンは一般に媒染剤との親和性も良くよく、その点からも好ましい。

【0057】媒染剤含有層のバインダーは硬膜されていることが好ましい。これによって、多量の水に対する耐水性をより向上させることができる。バインダーが未硬膜の場合、インク吸収時に上層の空隙層に膨潤したバインダーが侵入し、空隙を塞ぐことによりインク吸収性を低下させる傾向がある。

【0058】例えばバインダーとしてゼラチンを選択した場合、クロム明礬、ホルムアルデヒド、グリオキサール、エポキシ系化合物、ビニルスルホン系化合物、アクリロイル系化合物、s-トリアジン系化合物、N-メチロール系化合物、カルボジイミド系化合物、エチレンイミノ系化合物等の硬膜剤が周知である。又、バインダーとしてポリビニルアルコールを選択した場合、硼砂、硼酸、硼酸塩、レゾルシノール、カテコール、フロログルシノール、没食子酸、バナジン酸、蔞酸、N-メチロール等の硬膜剤が知られている。

【0059】本発明で用いられる水溶性染料に対する媒染剤としては、ポリエチレンイミン、特開昭57-36692号、同59-20696号、同59-33176号、同59-33177号、同59-96987号、59-155088号、同60-11389号、同60-49990号、同60-83882号、同60-109894号、同61-277484号、同61-293886号、同62-19483号、同62-198493号、同63-49478号、同63-115780号、同63-203896号、同63-274583号、同63-280681号、同63-260477号、特開平1-9776号、同1-24784号、同1-40371号、同3-133686号、同6-234268号、同7-125411号等に記載された1～3級のアミノ基又は4級アンモニウム基を有するポリマー又は化合物が好ましく用いられる。

【0060】これらの内、比較的耐光性の劣化が小さく、しかも強固な染料媒染性を有する媒染剤として、3級アミノ基又は4級アンモニウム基を有する塩基性のラテックス重合体を用いるのが好ましい。

【0061】本発明に好ましく用いられる3級又は4級窒素原子を有する塩基性ラテックス重合体は、下記一般式(L)で表される。

【0062】

一般式(L) (A) x - (B) y - (C) z

式中、Aは3級アミノ基又は4級アンモニウム基を有する共重合可能な単量体から誘導される繰返し単位を表し、Bは少なくとも2個のエチレン性不飽和基を有する共重合可能な単量体から誘導される繰返し単位を表し、

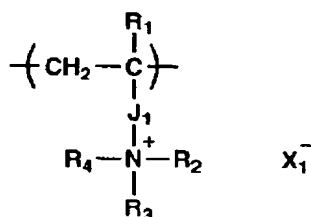
Cは少なくともA、B以外のエチレン性不飽和基を有する共重合可能な単量体から誘導される繰返し単位を表す。xは10～98モル%、yは0～10モル%、zは0～90モル%である。

【0063】一般式(L)において、Aは特に好ましくは下記一般式(LA-1)、(LA-2)、(LA-3)、(LA-4)又は(LA-5)で表される。

【0064】

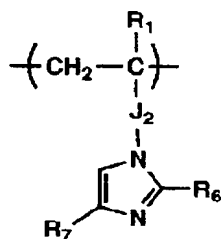
【化1】

### 一般式(LA-1)



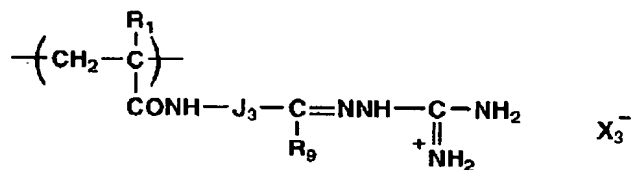
【0065】式中、R<sub>1</sub>は水素原子又は炭素原子数1～4のアルキル基を表す。J<sub>1</sub>は2価の連結基を表し、置換又は未置換のベンジル基又は－COY－を表す。Yは炭素原子数が1～20の2価の連結基であり、例えばアルキレン基、アリーレン基、－O－Y'－基、－NH－

### 一般式(LA-3)



【0069】式中、J<sub>2</sub>は単なる結合手又は2価の連結基（アルキレン基、アリーレン基、アラルキレン基等）を表す。R<sub>1</sub>は一般式（LA-1）のR<sub>1</sub>と同義であり、R<sub>6</sub>及びR<sub>7</sub>は各々、水素原子、アルキル基又はアラルキ

### 一般式(LA-5)



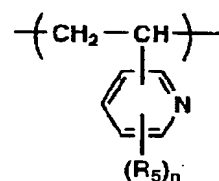
【0071】式中、R<sub>1</sub>は一般式(LA-1)のR<sub>1</sub>と同義であり、R<sub>9</sub>はアルキル基を表す。J<sub>3</sub>は単なる結合手又は2価の連結基(それぞれ置換基を有してもよいアルキレン基、アリーレン基又はアラルキレン基等)を表す。X<sub>3</sub><sup>-</sup>は陰イオンを表す。

Y'-基(Y'はアルキレン基、アリーレン基、アラルキレン基など)を表す。R<sub>2</sub>、R<sub>3</sub>及びR<sub>4</sub>は各々、炭素原子数1~18のアルキル基又は炭素原子数7~18のアラルキル基を表し、これらのアルキル基又はアラルキル基は置換基を有してもよい。X<sup>-</sup>は陰イオンを表し、例えばハロゲンイオン、アルキルスルホン酸イオン、アリールスルホン酸イオン、酢酸イオン等を表す。

【 0 0 6 6 】

【化2】

### 一般式(LA-2)

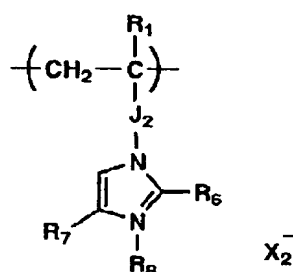


【0067】式中、R<sub>5</sub>は水素原子、アルキル基、アラ  
ルキル基又は水素原子を有するアルキル基を表し、nは  
1～4の整数を表す。nが2以上の時、複数のR<sub>5</sub>は同  
じでも異なってもよい。

【 0 0 6 8 】

【化3】

### 一般式(LA-4)



ル基を表す。R<sub>8</sub>はアルキル基又はアラルキル基を表す。X<sub>2</sub><sup>-</sup>は陰イオンを表す。

【 0 0 7 0 】

【化4】

【0072】一般式（LA-1）～（LA-5）で表される繰返し単位を形成する単量体の代表例を以下に示す。

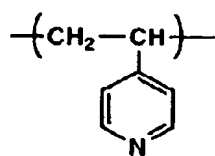
【 0 0 7 3 】

【化5】

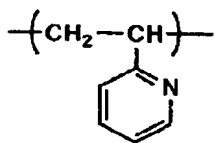


13

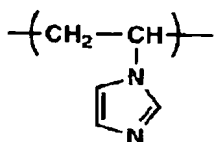
M-1



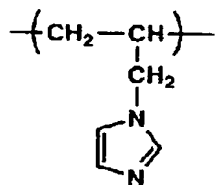
M-2



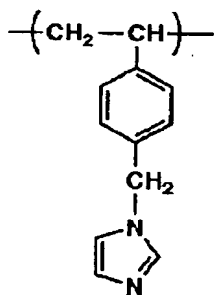
M-3



M-4



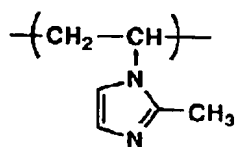
M-5



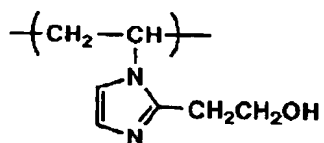
【0074】

14

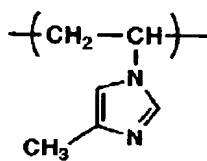
M-6



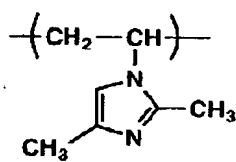
M-7



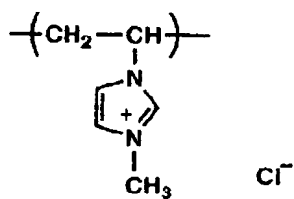
M-8



M-9



M-10

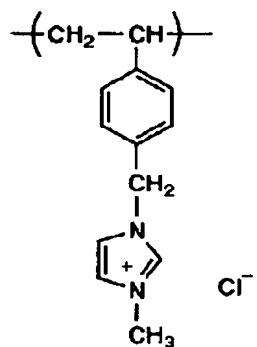


40

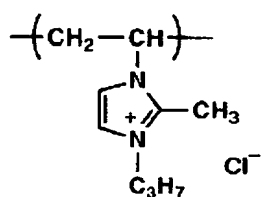
【化6】

15

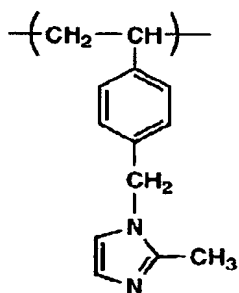
M-11



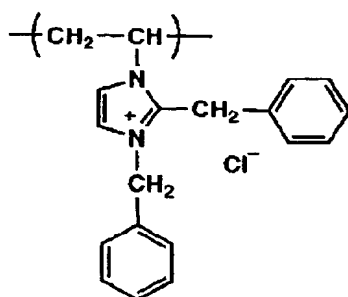
M-12



M-13

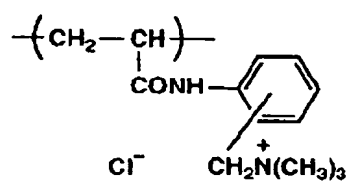


M-14

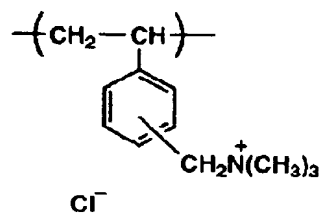


16

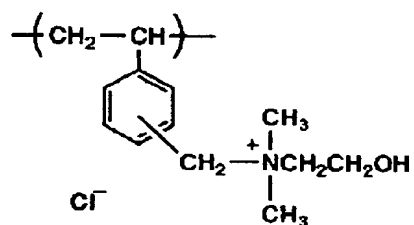
M-15



M-16



M-17



【0075】

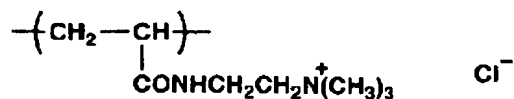
40

【化7】

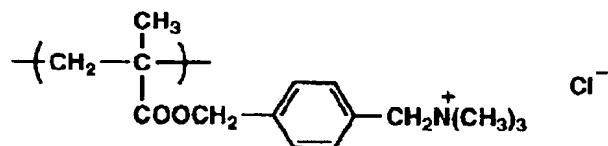
17

18

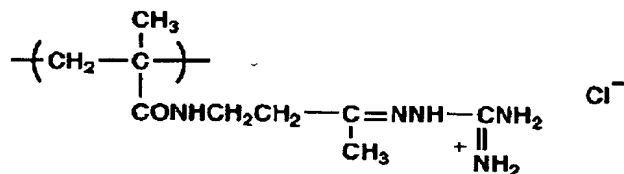
M-18



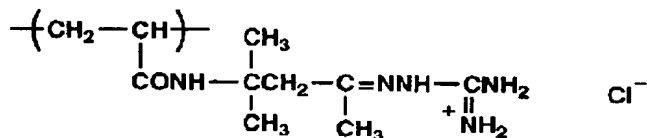
M-19



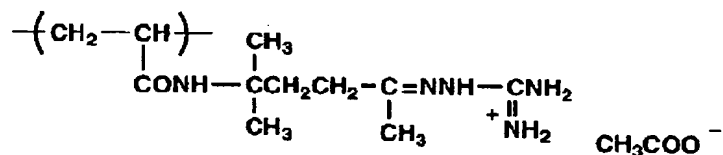
M-20



M-21



M-22



【0076】一般式(L)において、Bで表される繰返し単位を形成する単量体の例としては、ジビニルベンゼン、エチレングリコールジメタクリレート、トリメチロールプロパントリアクリレート、テトラメチレングリコールジアクリレート、プロピレングリコールジメタクリレート等が挙げられる。又、Cで表される繰返し単位を形成する単量体の例としては、エチレン、1-ブテン、スチレン、アクリル酸、メタクリル酸、メチルメタクリレート、エチルメタクリレート、ブチルアクリレート、

t-ブチルアクリレート、オクチルアクリレート、ベンジルアクリレート、アクリルニトリル、マレイン酸、酢酸ビニル、アクリルアミド及びヒドロキシメチルメタクリレート等が挙げられる。

【0077】一般式(L)で表される塩基性ラテックスの具体例を以下に示す。ただし、表中のA、B、Cは、それぞれ単量体で示した。

【0078】

【表1】

番号	A	B	C	x	y	z
L-1	M-1	—	C-2	70	0	25
			C-5			5
L-2	M-3	B-1	C-2	70	4	26
L-3	M-5	B-1	C-2	70	4	26
L-4	M-3	B-1	C-4	76	4	20
L-5	M-3	B-1	C-1	70	4	26
L-6	M-5	B-1	C-1	70	4	26
L-7	M-5	B-2	C-1	70	4	26
L-8	M-3	B-1	C-1	40	4	26
	M-12			30		
L-9	M-5	B-1	C-7	70	4	26
L-10	M-5	B-1	C-1	60	2	20
			C-5			18
L-11	M-11	B-1	C-2	70	4	26
L-12	M-15	—	C-2	60	—	40
L-13	M-15	B-1	C-2	60	2	38

【0079】

【表2】

番号	A	B	C	x	y	z
L-14	M-15	—	C-6	65	—	35
L-15	M-16	—	C-2	75	—	25
L-16	M-16	B-1	C-1	70	4	26
L-17	M-16	B-1	C-1	70	4	16
			C-4			10
L-18	M-18	B-1	C-1	70	3	15
			C-4			12
L-19	M-18	B-1	C-1	65	4	19
			C-5			12
L-20	M-18	B-1	C-3	60	4	36
L-21	M-21	—	C-6	60	—	40
L-22	M-21	B-1	C-4	60	2	38
L-23	M-22	—	C-8	60	—	40
L-24	M-22	—	C-4	60	—	40
L-25	M-22	—	C-6	60	—	40
L-26	M-22	B-1	C-8	60	—	40

【0080】表中のB-1～B-2、C-1～C-8は以下を示す。

【0081】B-1：ジビニルベンゼン  
 B-2：エチレングリコールジメタクリレート  
 C-1：スチレン  
 C-2：ブチルアクリレート  
 C-3：t-ブチルアクリレート  
 C-4：酢酸ビニル  
 C-5：ヒドロキシメチルメタクリレート  
 C-6：アクリルアミド  
 C-7：N-ビニルピロリドン  
 C-8：N-（2-アセチル-1,1,1-ジメチルエチ

20 ル）アクリルアミド

本発明における媒染剤の使用量は、記録用紙1m<sup>2</sup>当たり0.1～10g、好ましくは0.2～5g、特に好ましくは0.5～3gの範囲である。

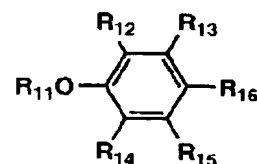
【0082】本発明に用いるインクジェット記録用紙は、水溶性染料の耐光性を向上させる目的で画像安定剤を含有させることが好ましい。画像安定剤は水溶性のものを選択して塗布液に混合してもよいし、油性のものを用いて塗布液に混合してもよい。

【0083】好ましい画像安定剤として、一般式（ST-I）及び（ST-II）で表される化合物が挙げられる。

【0084】

【化8】

一般式(ST-I)



40

【0085】式中、R<sub>11</sub>は水素原子、アルキル基、アルケニル基又はアリール基を表し、R<sub>12</sub>、R<sub>13</sub>、R<sub>14</sub>、R<sub>15</sub>及びR<sub>16</sub>は各々、水素原子、ハロゲン原子、シアノ基、ニトロ基、ヒドロキシル基、スルホ基又は1価の有機基を表す。

【0086】ただし、R<sub>11</sub>が水素原子の場合、R<sub>12</sub>及びR<sub>14</sub>が同時に水素原子であることはない。又、R<sub>11</sub>がアルキル基、アルケニル基又はアリール基である場合、R<sub>12</sub>、R<sub>13</sub>、R<sub>14</sub>、R<sub>15</sub>及びR<sub>16</sub>の少なくとも一つは、OR<sub>17</sub>（R<sub>17</sub>はアルキル基又はアルケニル基）又は-N

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21

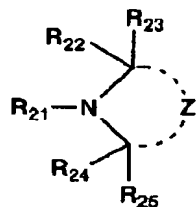
(R<sub>28</sub>) R<sub>29</sub>、(R<sub>28</sub> 及び R<sub>29</sub> は各々、水素原子、アルキル基又はアルケニル基) である。

【0087】 R<sub>11</sub> と R<sub>12</sub>、R<sub>12</sub> と R<sub>13</sub>、R<sub>13</sub> と R<sub>16</sub>、R<sub>16</sub> と R<sub>15</sub>、R<sub>15</sub> と R<sub>14</sub>、R<sub>14</sub> と R<sub>11</sub> は各々、互いに結合して環を形成してもよい。

【0088】

【化9】

一般式(ST-II)



22

【0089】 式中、R<sub>21</sub> は水素原子、アルキル基、アルケニル基、フェニル基、ヒドロキシル基、スルホニル基、スルフィニル基又はアシル基を表し、R<sub>22</sub>、R<sub>23</sub>、R<sub>24</sub> 及び R<sub>25</sub> は各々、水素原子又はアルキル基を表す。Z は5～7員の含窒素複素環を形成するのに必要な非金属原子群を表す。

【0090】 R<sub>21</sub> と R<sub>22</sub>、R<sub>22</sub> と R<sub>23</sub>、R<sub>24</sub> と R<sub>25</sub>、R<sub>24</sub> と R<sub>21</sub> は各々、互いに結合して環を形成してもよい。

【0091】 本発明に用いる特に好ましい画像安定剤の例を以下に示す。

【0092】

【化10】

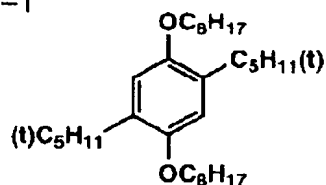
20

30

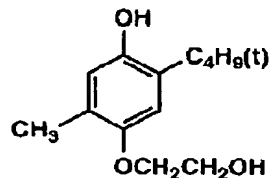
40

23

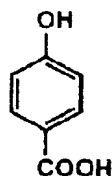
ST-1



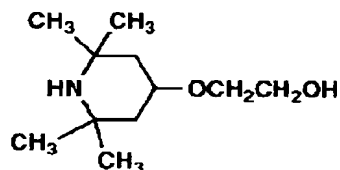
ST-3



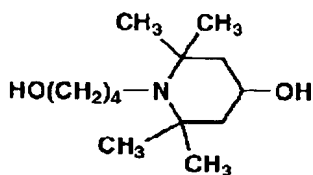
ST-5



ST-7

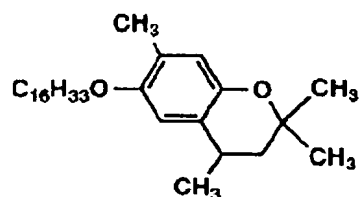


ST-8

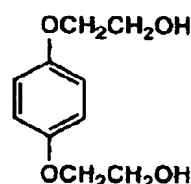


24

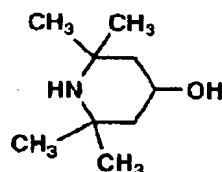
ST-2



ST-4



ST-6



【0093】インクジェット記録用紙は、水溶性染料の耐光性を向上させる目的で紫外線を吸収する化合物を含有させることができる。紫外線を吸収する化合物としては、例えば特開昭57-74193号、同57-87988号及び同62-261476号等に記載の紫外線吸収剤が挙げられる。媒染剤層に存在する水溶性染料に紫外線が到達しないようにするには、これらの紫外線吸収剤を媒染剤層よりも支持体から見て遠い層に含有させるのが効果的である。

【0094】インクジェット記録用紙のインク受容性層側の任意の層中には、必要に応じて更に各種の添加剤を含有させることができる。例えば、アニオン、カチオン又はノニオンの各種界面活性剤、特開昭59-4299

3号、同59-52689号、同62-280069号、同61-242871号及び特開平4-219266号等に記載される蛍光増白剤、硫酸、磷酸、枸橼酸、水酸化ナトリウム、水酸化カリウム、炭酸カリウム等のpH調整剤、消泡剤、ジエチレングリコール等の潤滑剤、防腐剤、増粘剤、硬膜剤、帯電防止剤、マツト剤等、公知の添加剤を含有させることもできる。

【0095】インクジェット記録用紙におけるインク記録面側の塗布固形分の量は特に制限はないが、概ね5～60g/m<sup>2</sup>が好ましく、10～40g/m<sup>2</sup>がより好ましい。なお、記録画像形成後のカール防止という面からは、成る可く薄く形成するのが好ましい。

【0096】インクジェット記録用紙の支持体として

は、従来、インクジェット用記録用紙として公知のもの内、水を実質的に全く吸収しない支持体を適宜使用できる。

【0097】透明支持体としては、ポリエステル系樹脂、ジアセテート系樹脂、トリアセテート系樹脂、アクリル系樹脂、ポリカーボネート系樹脂、ポリ塩化ビニル系樹脂、ポリイミド系樹脂、セロハン、セルロイド等の材料から成るフィルムなどが挙げられ、この中でもOHPとして使用された時の輻射熱に耐える性質のものが好ましく、ポリエチレンテレフタレート（PET）が特に好ましい。透明支持体の厚さとしては、約10～200μmが好ましい。支持体のインク受容層側及びバック層側には、公知の下引層を設けることが、インク受容層やバック層と支持体との接着性の観点から好ましい。

【0098】又、不透明の支持体としては、基紙の少なくとも一方に白色顔料等を添加したポリオレフィン樹脂被覆層を有する樹脂被覆紙（所謂RCペーパー）、PETに白色顔料を添加して成る所謂ホワイトペットが好ましい。

【0099】親水性層を支持体上に塗布する方法は、公知の方法から適宜選択して行うことができる。好ましい方法は、ゼラチンの様なゾルゲル変換可能な親水性バインダーを含む塗布液を支持体上に塗設・乾燥して得るものである。親水性バインダー層は2層以上あってもよく、この場合、2層以上を同時に塗布することもでき、特に全ての親水性バインダー層を1回の塗布で済ます同時塗布が好ましい。

【0100】例えば特開平6-64306号に記載されるような、ゼラチン等、ゾルゲル変換可能な親水性バインダー含有インク受容層を支持体上に塗布後、冷却してゲル状態にした後、コールドドライ法で乾燥する方法は好ましい方法の一つである。

【0101】塗布方式としては、ロールコーティング法、ロッドバーコーティング法、エアナイフコーティング法、スプレーコーティング法、カーテン塗布法あるいは米国特許2,681,294号に記載のホッパーを使用するエクストルージョンコート法が好ましく用いられる。

【0102】インクジェット記録方法に用いるインクの吐出方式は、水溶性インクを吐出可能なインクジェット記録方式であればよく、例えば中村孝一編著「インク・ジェット記録技術の動向」（日本科学情報社刊、199

5）1～14頁に記載の連続噴射荷電制御方式やオンデマンド方式等の記録方式を用いることができる。これらの中でも、オンデマンド方式の記録方式に適用して使用することにより、より大きな効果を得ることができる。

【0103】水溶性インクとは、水溶性染料を主な発色源として含有し、水と親水性溶媒を含有するインクである。

【0104】本発明におけるインク最大吐出量とは、本発明に用いるインクジェットプリンタが通常のあらゆる画像を出力する時に使用しうる単位面積当たりのインク体積量の最大値である。例えばカラー画像用のプリンタの場合、イエロー、マゼンタ、シアン、ブラック各単色の最高濃度を得るためのインク量を足し合わせたものが、必ずしもインク最大吐出量ではない。

【0105】インク最大吐出量は、インク液滴1滴の体積が既知で、画像を形成するための液滴の配列方法が既知であれば計算によって求めることができる。

【0106】

【実施例】以下に本発明の実施例を挙げて説明するが、本発明はこれらに限定されるものではない。なお、実施例中の「%」は特に断りのない限り絶対重量%を示し、添加量はインクジェット記録用紙1m<sup>2</sup>当たりの量を示す。

【0107】100g/m<sup>2</sup>の原紙両面をポリエチレンで被覆した紙支持体（厚さ140μm、記録面側のポリエチレン層中に7重量%のアナターゼ型二酸化チタン含有し、記録面の裏面側にバック層としてアルカリ処理ゼラチン1.2g/m<sup>2</sup>と硬膜剤を含有する層を有する）上の記録面側に、それぞれ表3、4、5及び6に示す組成の塗布液を多層同時塗布・乾燥し、表中の乾燥膜厚及び空隙容量になるように調整して記録用紙1～11を得た。

【0108】なお、記録用紙中の空隙容量は以下のようにして求めた。即ち、試料の断面を光学顕微鏡・電子顕微鏡等で観察し、インク受容層の層厚を測定する。該インク受容層の組成から固形分の体積を知ることができるので、空隙ができていないとした時の層厚を計算できる。この測定値と計算値の差が空隙によって増加した層厚であるので、計算によってその空隙容量を知ることができる。

【0109】

【表3】

記録用紙 1			
上層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 界面活性剤-1 界面活性剤-2	790ml 40g 25g 0.7g 0.3g	乾燥膜厚 0.5μm
中層	純水 炭酸カルシウム（平均粒径：約0.07μm） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	500ml 192g 12.8g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤-1 界面活性剤-1 界面活性剤-2	790ml 40g 25g 10g 0.7g 0.3g	乾燥膜厚 2.0μm
記録用紙 2			
上層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 界面活性剤-1 界面活性剤-2	790ml 40g 25g 0.7g 0.3g	乾燥膜厚 0.5μm
中層	純水 微粒子シリカ（平均粒径：約0.07μm） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2g 12.8g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 PCゼラチン（アミノ基封鎖率：約88%） PVA 媒染剤-1 界面活性剤-1 界面活性剤-2	790ml 40g 25g 10g 0.7g 0.3g	乾燥膜厚 2.0μm

PCゼラチン：フェニルカルバモイル化ゼラチン

PVA：ポリビニルアルコール

【0110】

【表4】



記録用紙 3			
上層	純水	790ml	乾燥膜厚 2.0 $\mu\text{m}$
	PCゼラチン (アミノ基封鎖率: 約88%)	40 g	
	PVA	25 g	
	媒染剤-1	10 g	
	界面活性剤-1	0.7 g	
	界面活性剤-2	0.3 g	
下層	純水	980ml	空隙容量 20ml/ $\text{m}^2$
	微粒子シリカ (平均粒径: 約0.07 $\mu\text{m}$ )	48.2 g	
	PVA (鹸化度: 89%, 平均重合度: 2,350)	12.8 g	
	界面活性剤-3	1.2 g	

記録用紙 4			
上層	純水	980ml	空隙容量 20ml/ $\text{m}^2$
	微粒子シリカ (平均粒径: 約0.07 $\mu\text{m}$ )	48.2 g	
	PVA (鹸化度: 89%, 平均重合度: 2,350)	12.8 g	
	界面活性剤-3	1.2 g	
下層	純水	790ml	乾燥膜厚 2.0 $\mu\text{m}$
	PCゼラチン (アミノ基封鎖率: 約88%)	40 g	
	PVA	25 g	
	媒染剤-1	10 g	
	界面活性剤-1	0.7 g	
	界面活性剤-2	0.3 g	

記録用紙 5			
上層	純水	980ml	空隙容量 20ml/ $\text{m}^2$
	微粒子シリカ (平均粒径: 約0.07 $\mu\text{m}$ )	48.2 g	
	PVA (鹸化度: 89%, 平均重合度: 2,350)	12.8 g	
	界面活性剤-3	1.2 g	
下層	純水	790ml	乾燥膜厚 2.0 $\mu\text{m}$
	PCゼラチン (アミノ基封鎖率: 約88%)	40 g	
	PVA	25 g	
	媒染剤-1	10 g	
	界面活性剤-1	0.7 g	
	界面活性剤-2	0.3 g	

【0111】

【表5】

記録用紙 6			
上層	純水 微粒子シリカ (平均粒径: 約0.07 $\mu\text{m}$ ) PVA (鹸化度: 89%, 平均重合度: 2,350) 界面活性剤-3	930ml 140 g 12.8 g 1.2 g	空隙容量 20ml/ $\text{m}^2$
下層	純水 PCゼラチン (アミノ基封鎖率: 約88%) PVA 媒染剤-1 界面活性剤-1 界面活性剤-2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu\text{m}$
記録用紙 7			
上層	純水 微粒子シリカ (平均粒径: 約0.07 $\mu\text{m}$ ) PVA (鹸化度: 89%, 平均重合度: 2,350) 界面活性剤-3	980ml 48.2 g 12.8 g 1.2 g	空隙容量 20ml/ $\text{m}^2$
下層	純水 PCゼラチン (アミノ基封鎖率: 約88%) PVA 媒染剤-2 界面活性剤-1 界面活性剤-2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu\text{m}$
記録用紙 8			
上層	純水 微粒子シリカ (平均粒径: 約0.07 $\mu\text{m}$ ) PVA (鹸化度: 89%, 平均重合度: 2,350) 界面活性剤-3	980ml 48.2 g 12.8 g 1.2 g	空隙容量 20ml/ $\text{m}^2$
下層	純水 酸処理ゼラチン PVA 媒染剤-1 界面活性剤-1 界面活性剤-2	790ml 40 g 25 g 10 g 0.7 g 0.3 g	乾燥膜厚 2.0 $\mu\text{m}$

【0112】

【表6】

記録用紙9			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2g 12.8g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 酸処理ゼラチン PVA 媒染剤-1 硬膜剤-1 界面活性剤-1 界面活性剤-2	790ml 40g 25g 10g 2g 0.7g 0.3g	乾燥膜厚 2.0 $\mu$ m
記録用紙10			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 界面活性剤-3	980ml 48.2g 12.8g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 酸処理ゼラチン PVA 媒染剤-1 画像安定剤（例示ST-5） 硬膜剤-1 界面活性剤-1 界面活性剤-2	780ml 40g 25g 10g 10g 2g 0.7g 0.3g	乾燥膜厚 2.0 $\mu$ m
記録用紙11			
上層	純水 微粒子シリカ（平均粒径：約0.07 $\mu$ m） PVA（鹸化度：89%，平均重合度：2,350） 分散物-1 界面活性剤-3	980ml 48.2g 12.8g 5g 1.2g	空隙容量 20ml/m <sup>2</sup>
下層	純水 酸処理ゼラチン PVA 媒染剤-1 硬膜剤-1 界面活性剤-1 界面活性剤-2	780ml 40g 25g 10g 2g 0.7g 0.3g	乾燥膜厚 2.0 $\mu$ m

【0113】記録用紙作製に用いられた素材の構造は以下の通りである。

【0114】  
【化11】

$$\text{C}_8\text{H}_{17}\text{SO}_2-\text{NCH}_2\text{COOK}$$

|  
 $\text{C}_3\text{H}_7$

$$\text{C}_8\text{H}_{17}\text{SO}_2\text{NH}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_3 \quad \text{Br}^-$$
$$\text{NaO}_3\text{S}-\text{CH}(\text{COOCH}_2(\text{CF}_2\text{CF}_2)_3\text{H})\text{COOCH}_2(\text{CF}_2\text{CF}_2)_4\text{H}$$
$$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})_{70}\text{---}(\text{CH}_2\text{---CH})_{26}\text{---}(\text{CH}_2\text{---CH})_4\text{---} \\ | \qquad \qquad \qquad | \qquad \qquad \qquad | \\ \text{C}_6\text{H}_4 \qquad \qquad \text{C}_6\text{H}_5 \qquad \qquad \text{C}_6\text{H}_4 \\ | \qquad \qquad \qquad | \qquad \qquad \qquad | \\ \text{CH}_2 \qquad \qquad \qquad \text{---}(\text{CH---CH}_2)\text{---} \\ | \\ \text{N} \\ \text{N} \end{array}$$
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{---}(\text{CH}_2-\text{CH})_{98}(\text{CH}_2-\text{C})_2\text{---} \\ | \qquad \qquad \qquad | \\ \text{C}_6\text{H}_4 \qquad \qquad \text{COOCH}_2\text{---OOC} \\ | \qquad \qquad \qquad | \\ \text{CH}_2\text{N}^+(\text{CH}_3)_3 \qquad \text{---}(\text{CH}_2-\text{C})\text{---} \\ \qquad \qquad \qquad | \\ \qquad \qquad \qquad \text{CH}_3 \\ \text{Cl}^- \end{array}$$
c1ccc2c(c1)nnc2-c3cc(O)ccc3C4CCCCC4

【0119】《耐水性》印字試料を20℃の水の中に1

0分間浸漬した後、乾燥し、マゼンタ色の最高濃度部分の印字画像の耐水性を残存濃度で比較した。濃度が高いものを◎、低いものを×の4段階で評価した。

【0120】《耐湿性》印字後の試料を23℃・相対湿度20%で2週間保存した後、60℃・相対湿度80%で3日間保存して各色の滲み度合いを調べた。

【0121】評価は、60℃・相対湿度80%に保存前後での線の拡がりを下記の基準で目視判定した。

【0122】

◎：全く滲み無し

○：滲み幅が約0.1mm未満（視感的には滲みが僅かに認められる程度）

△：滲み幅が0.1mm～0.5mm未満（視感的には許容不可）

×：滲み幅が0.5mm以上（殆ど画像としての価値が

ないレベル）

《乾燥性》印字後2分後に、印字面に対し同じ記録用紙の裏面を重ね合わせ、100g/cm<sup>2</sup>の加重をかけて1分間放置し、裏面に転写したインクの度合いを下記の基準で目視判定した。

【0123】

◎：全く転写なし

○：微かに転写があるが、原画像に殆ど影響なし

×：多量のインクが転写し、原画像は観賞に堪えない

10 《濃度ムラ》印字試料のベタ部をマイクロデンストメーター（アパーチャー径：200μm）で20点濃度測定し、濃度値の標準偏差を求めた。

【0124】

【表7】

記録用紙No.	耐光性	耐水性	耐湿性	乾燥性	濃度ムラ
1(本発明)	60	△	○	○	0.4
2(本発明)	75	△	○	○	0.6
3(比較例)	30	○	○	○	0.9
4(比較例)	25	×	×	×	1.5
5(本発明)	75	△	△	○	0.1
6(本発明)	80	△	△	◎	0.0
7(本発明)	75	△	○	○	0.1
8(本発明)	70	○	○	○	0.1
9(本発明)	70	◎	○	○	0.1
10(本発明)	90	◎	○	○	0.1
11(本発明)	95	◎	○	○	0.1

【0125】

【発明の効果】以上の結果から、本発明により、耐光・

30 耐水・耐湿性に優れ、かつ濃度ムラの少ない高品位のインクジェット記録画像を提供することが可能となった。